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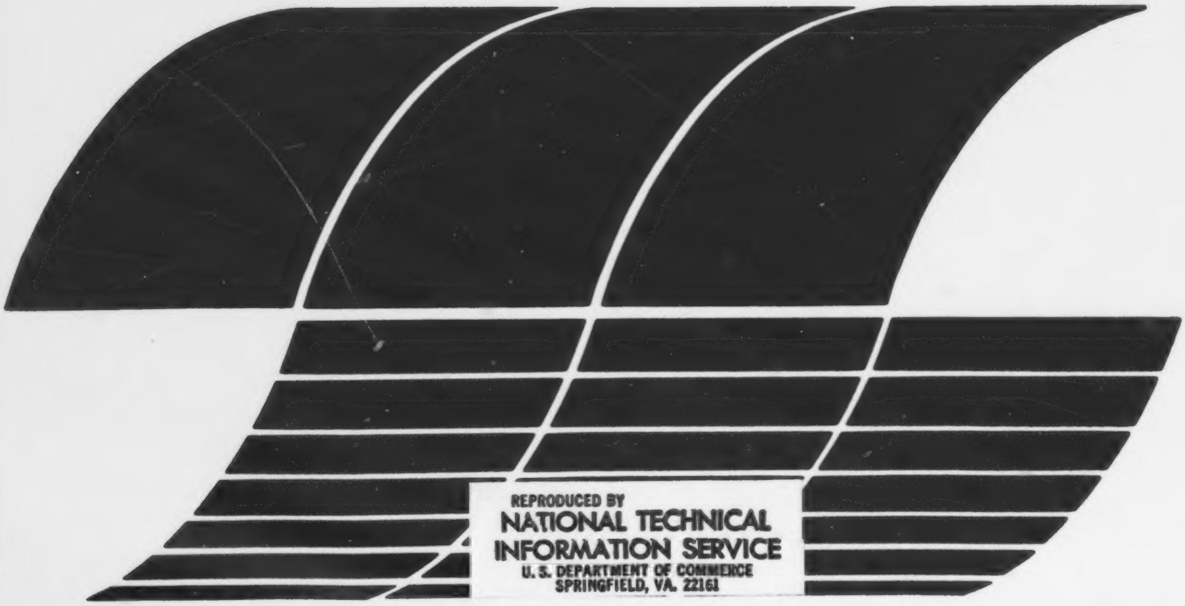

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16. ABSTRACT

The report gives results of a study of a potassium scrubbing system that recovers useful forms of sulfur from pollutants while utilizing a low-energy process to regenerate the absorbing medium. The report also describes two versions of a new, regenerable process for SO2 scrubbing that show promise for further development; they are based on absorption in a melamine slurry, followed by low temperature thermal or chemical regeneration. No solids requiring disposal are generated by the potassium scrubbing system. Laboratory tests of the scrubbing, thermal decomposition, and reduction steps show that the process (based on the precipitation of potassium pyrosulfite) is feasible. The absorbing solution is regenerated by thermal stripping of one-third of the pyrosulfite and chemical reduction of the remainder to form hydrogen sulfide. Elemental sulfur is obtained via the Claus reaction. The report includes studies of the oxidation of various sulfite compounds produced in several different SO2 scrubbing processes. Using laboratory, bench-scale equipment of new design, the sulfites of ammonia, potassium, zinc, and calcium were successfully oxidized with high efficiency. Such oxidation will be beneficial to the value of the products and to improve physical properties or reduce chemical oxygen demand of the waste.

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Desulfurization	Regeneration	Phosphate Fertilizer	07A,07D	
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Potassium	Hydrogen Sulfide	Claus Reaction	07B	
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Advanced Concepts: SO_2 Removal Process Improvements

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise, and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The Tennessee Valley Authority contributes to this multidisciplinary focus through programs engaged in investigations of

- chemical and physical characteristics of process emissions and secondary pollutants formed in the biosphere, and their measurement,
- mechanisms governing the movement of these residuals through the biosphere, and their potential for impacting human health and safety,
- effects of process residuals in combination with natural phenomena on terrestrial and aquatic receptors,
- mitigation alternatives and beneficial uses of residuals, and

a search for economic processes and management alternatives to prevent environmental damages and to reclaim values from process residuals.

This report presents data from a study of a potassium scrubbing system that will result in the production of useful forms of sulfur from pollutants while utilizing a low-energy process for regeneration of the absorbing medium. No solids for disposal are generated in the recovery process. Also included in the report are studies of the oxidation of some sulfites that might be formed in sulfur dioxide scrubbing processes. Such oxidation would be beneficial to improve the value of the products, to improve the physical properties of the products, and/or to reduce the chemical oxygen demand of the products. Also studied were the use of weak sulfuric acid resulting from some sulfur dioxide scrubbing processes and the concentration of the products of that use. Two processes for use of melamine to remove sulfur dioxide from stack gas were studied.

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EXECUTIVE SUMMARY

Interest in regenerative potassium scrubbing processes results from the favorable solubility relationship in this system; potassium pyrosulfite, heavily loaded with SO_2, can be precipitated from scrubber effluent. Laboratory studies indicated excellent SO_2 removal from stack gas but indicated difficulty in precipitating potassium pyrosulfite unless a cooling step is used to cause precipitation. Antioxidants were helpful in controlling oxidation during scrubbing. Laboratory studies of thermal decomposition of potassium pyrosulfite indicated disproportionation to potassium sulfate, thiosulfate, and sulfide occurred to the extent that appreciable sulfate removal would need to be provided. Laboratory studies of the reduction of potassium sulfate indicated that efficient reduction might be difficult but that a process might be technically feasible which involved potassium scrubbing, evolution of one-third of the sulfur as SO_2 by thermal decomposition, reduction of two-thirds to hydrogen sulfide, and reaction of these to elemental sulfur by the Claus process.

In laboratory oxidation studies, a gas-liquor contacting device was developed that appeared superior to a spinning cup oxidizer developed in Japan. Conditions were defined for oxidation of sulfites of ammonia, potassium, zinc, and calcium. Bench-scale studies indicated that increasing the depth of submergence of the contactor up to 2 feet improved oxidation but further increases were less helpful.

Laboratory studies indicated that sulfate could be selectively precipitated from soluble alkali scrubbing systems by precipitation with barium salts; barium sulfate formed could be processed into elemental sulfur by commercially practiced methods.

Laboratory studies of extraction of phosphate rocks with dilute sulfuric acid indicated some promise for utilization of acid from stack gas recovery processes for acidulation of unbeneficiated phosphate matrix to produce dilute phosphoric acid.

Laboratory studies were made of freeze crystallization of ice from dilute phosphate systems which might be made by extraction of phosphate rock with dilute sulfuric acid recovered from stack gas scrubbing systems. Results indicated that a freeze concentration procedure, with continuous countercurrent washing of ice, might be used to attain P_2O_5 concentrations of 20 to 25% in either dilute phosphoric acid or ammonium phosphate systems; these concentrations should be usable. Water removal by freeze crystallization should be much more energy efficient than evaporation.

Melamine sulfite is very easy to decompose to melamine and SO_2 and can be formed by slurry scrubbing with melamine or by reaction of melamine with alkali bisulfite solution. Two possibly improved SO_2 recovery processes were identified for further development.

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We gratefully acknowledge the efforts of the secretarial staff, particularly Mrs. Martha Witt, who typed this report in accordance with EPA format.

POTASSIUM SCRUBBING

INTRODUCTION

Several attempts have been made to take advantage of the unique solubility relationship between potassium sulfite and potassium bisulfite (potassium metabisulfite or potassium pyrosulfite) in a regenerable SO_2 recovery process. The more acid bisulfite salt is less soluble than the sulfite at temperatures below about 80°C (see Figure 1). The attempts largely have been abandoned for several reasons including unwanted oxidation in the process, disproportionation in the regeneration step, and high energy requirements for recovering the sulfur value in both the regeneration and reduction steps. A generalized flowsheet is given in Figure 2.

Desired reactions occurring at various points in the process are given below.

Scrubber

$$K_2SO_3 + SO_2 \longrightarrow K_2S_2O_5$$

Decomposer

$$K_2S_2O_5 \xrightarrow[\Delta]{} K_2SO_3 + SO_2$$

If these were the only reactions, the process would be very simple and the reduction step would not be needed. However, some oxidation takes place in the scrubber. This reaction, $K_2SO_3 + 1/2O_2 \longrightarrow K_2SO_4$, forms the sulfate which will not react with SO_2 in the scrubber and necessitates the removal of sulfate from the system, either by bleeding a fairly expensive potassium stream or by reduction to a form suitable for absorption of SO_2.

In the decomposition step, a complicated disproportionation of the sulfur species takes place. Instead of the simple dissociation of $K_2S_2O_5$, there occurs a redistribution of oxygen among the sulfur atoms and compounds containing sulfate, sulfite, sulfide, polysulfides, thionates, etc. are formed. Of these, the sulfate is predominant.

In the reduction step, the potassium-sulfur salts are reduced to the sulfides. There is some volatilization of potassium sulfide; however, the off-gas stream from the reduction furnace may, in part, be used in the hydration-carbonation reactor where it would be recovered. Reactions occurring would be:

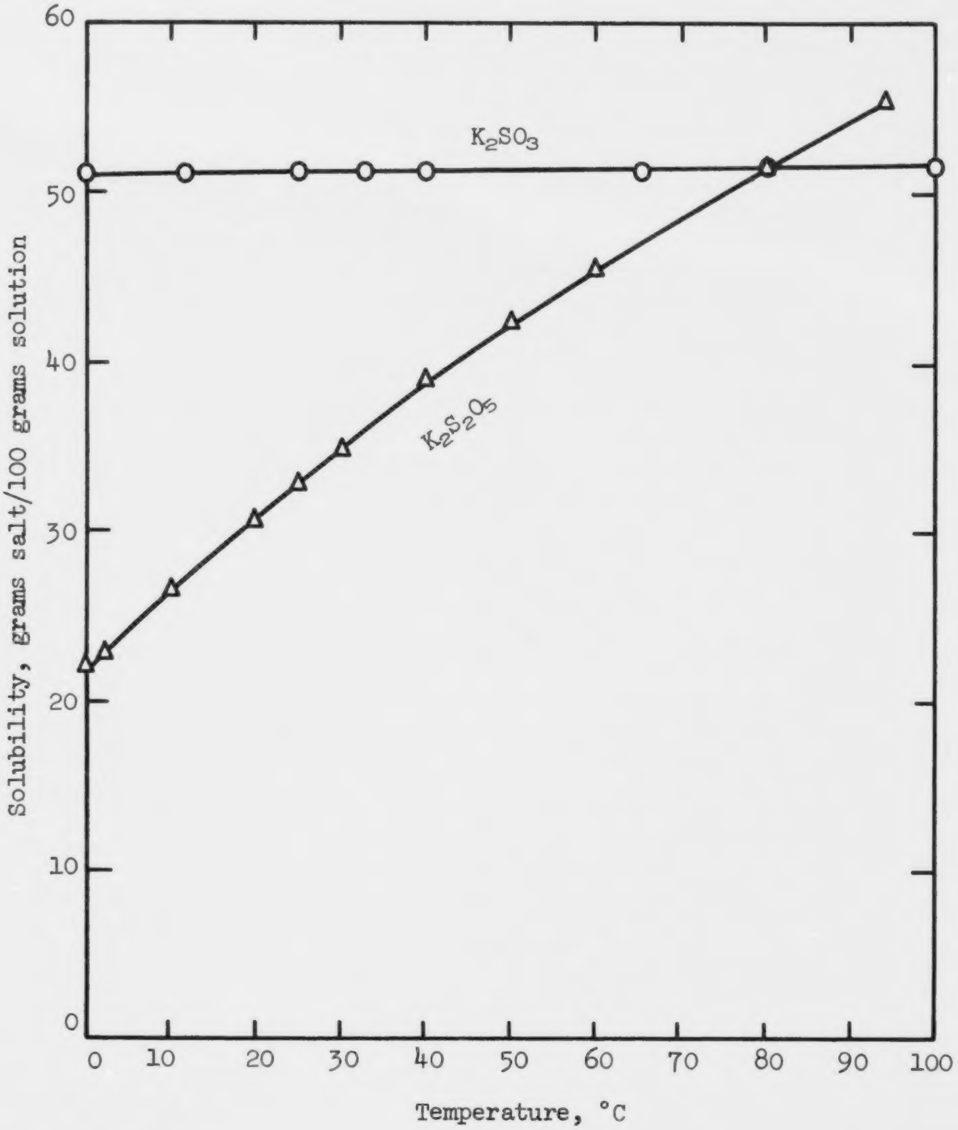
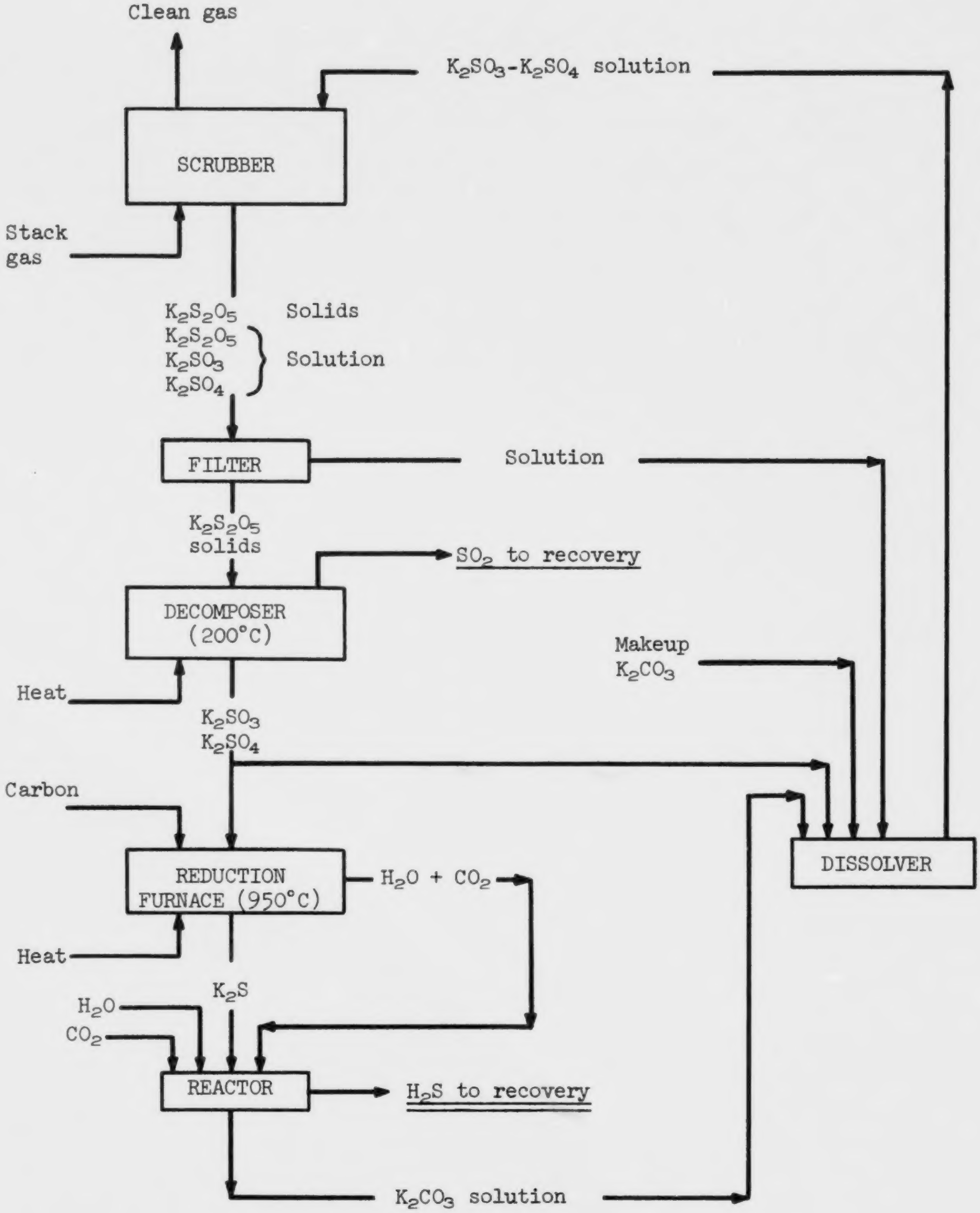


Figure 1. Solubility of K_2SO_3 and $K_2S_2O_5$ in water. (1)



Clean gas
K_2SO_3-K_2SO_4 solution
SCRUBBER
Stack gas
$K_2S_2O_5$ Solids
$K_2S_2O_5$
K_2SO_3
K_2SO_4
Solution
FILTER
Solution
$K_2S_2O_5$ solids
SO_2 to recovery
DECOMPOSER (200°C)
Heat
Makeup K_2CO_3
K_2SO_3
K_2SO_4
Carbon
DISSOLVER
REDUCTION FURNACE (950°C)
$H_2O + CO_2$
Heat
K_2S
H_2O
CO_2
REACTOR
H_2S to recovery
K_2CO_3 solution

Figure 2. Potassium scrubbing system for removal of sulfur oxides from waste gas streams--general flowsheet.

$$K_2SO_4 + 2C \longrightarrow 2CO_2 + K_2S$$

$$K_2S + 2H_2O \longrightarrow 2KOH + H_2S$$

$$2KOH + CO_2 \longrightarrow K_2CO_3$$

The scale of the reduction loop in the process would be dependent upon the amount of sulfate formed in the scrubber and the amount of disproportionation occurring in the thermal decomposer. Since the reduction step is included only to recover potassium in a form suitable for scrubbing and is expensive in both energy and investment costs, it is desired to limit the amount of material requiring reduction to as small a quantity as is practical. Means of accomplishing this reduction in quantity include supression of oxidation in the scrubber, such as limiting excess air in the plant boiler or including antioxidants in the scrubber and finding some operating procedure or additive in the decomposition step to limit disproportionation.

The test program was begun with a factorial study of the decomposition step.

THERMAL DECOMPOSITION OF POTASSIUM METABISULFITE

The problem of disproportionation appeared to be of greatest concern and to affect most the proportion of the regenerator product that would have to be directed through the reduction step.

There has been some conjecture that the disproportionation reaction might be dependent, in part, on the presence of the sulfur dioxide liberated in the decomposition process. In previous tests of open-air and vacuum heating of potassium metabisulfite, reported in the December 1968 report of the Applied Research Branch, Division of Chemical Development, Tennessee Valley Authority, up to half of the sulfur was volatilized in useful form but an excessive amount of the sulfur remaining in the residue was in the unwanted sulfate form. Later (November 1970 report) tests were made to determine whether sweeping liberated sulfur dioxide away with carrier gases might decrease sulfate formation. In tests with nitrogen, carbon dioxide, or air as sweep gas in a fluidized bed, about 45% of the sulfur was volatilized at 200° to 370°C but sulfate formation still was excessive. Lowest sulfate formation was obtained with humidified nitrogen as the sweep gas, but about 22% of the input sulfur was converted to sulfate or to equally undesirable thiosulfate.

In the current work, a first study was made in which reagent-grade potassium metabisulfite was subjected to a series of factorially designed tests in which it was heated in a glass vessel in a pot furnace to various temperatures, for varying times, with varying amounts of a sweep gas (N_2) being directed over or through the bed of material.

Test Plan and Equipment

The equipment used in the tests is shown in Figure 3. Test temperature was controlled by adjusting the temperature of the pot furnace; the temperatures of the furnace and sample were measured and recorded using the thermo-

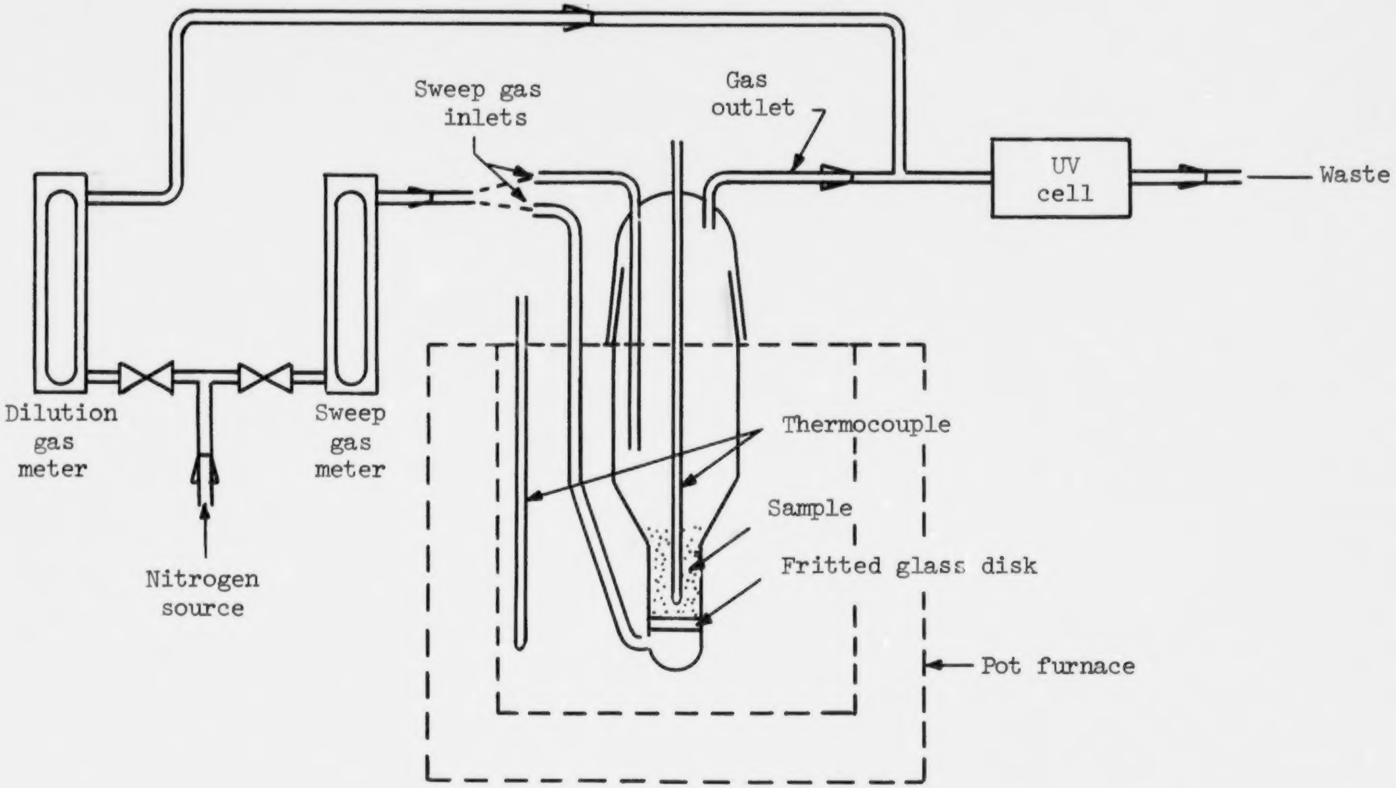

Sweep gas inlets
Gas outlet
UV cell
Waste
Dilution gas meter
Sweep gas meter
Nitrogen source
Thermocouple
Sample
Fritted glass disk
Pot furnace

Figure 3. Thermal decomposition of $K_2S_2O_5$--laboratory test equipment arrangement.

couples shown. The sweep gas was metered and passed either through the bed (through the fritted glass disc) or into the gas space above the bed by opening the appropriate gas inlet line. The alternate gas inlet was sealed. Off-gases were analyzed for SO_2 using the UV (ultraviolet) analyzer after dilution with a measured amount of N_2 which was added to keep the SO_2 concentration within the limits of the analyzer.

Using this equipment, a factorial test series was made in which the following conditions were imposed.

Variable	Limit Lower (-)	 Upper (+)
A - Furnace temperature, °C	168	204
B - Bed condition (gas direction)	Static	Fluidized
C - Time, min	15	30
D - Sweep gas rate, l/min	2.5	3

Responses measured were (1) the temperature attained in the product bed, (2) the weight loss of the product, (3) the area of the curve of the UV recorder chart to measure sulfur dioxide in the off-gas, and (4) the chemical analysis of the product. From the chemical analyses of the raw material and products, the following indices were calculated, assuming no K_2O loss: (1) the final weight of the product, (2) total sulfur loss, % of total sulfur input (% TS), (3) reduction in sulfite sulfur content, % TS, (4) disproportionation, % TS (which is the difference in the apparent losses of sulfite sulfur and total sulfur species), (5) the increase in sulfide sulfur, % TS, (6) the increase in thiosulfate sulfur, % TS, (7) the increase in sulfate sulfur (by difference), % TS, (8) the total sulfur loss, expressed as SO_2, % of input weight, and (9) the weight loss (K_2O balance), % of input weight. In a later series of tests, some P_2O_5 was added to determine its effect. Responses to show P_2O_5 recovery were calculated also. For the main body of data there were, then, 12 responses measured. Results of the tests are given in Table 1 along with calculations made from the chemical analyses of the residual solids and the statistical analyses of the several responses calculated or measured.

Evaluation of Data

The statistical analysis was made by the method suggested by Davies (2) but modified so that the values shown are the differences in the responses due to the various treatments; included also are the minimum values for which these differences are significant at the 90, 95, and 99% confidence levels. As an illustration, under the response column headed "Bed temperature, °C," it will be noted that there is a 90% confidence that any difference in response greater than 2.569°C is a real effect of the variable or interaction, a 95% confidence in differences greater than 3.277°C, and a 99% confidence in differences greater than 5.140°C. For convenience, all differences with 90% confidence or greater than the effect is real are underlined. Thus, in the "Bed temperature, °C" column, it is seen that the furnace temperature variation from about 170°C to 205°C caused a variation in bed temperature of

TABLE 1. THERMAL DECOMPOSITION OF POTASSIUM METABISULFITE

FACTORIAL TEST 1--DATA AND ANALYSIS

		Test conditions				Responses																	
									Chemical analysis, % by wt.							% of input sulfur						% of input weight	
									Sulfur										Increase in				
Plan position	Test No.	Furnace temp., °C	Bed condition[a]	Time, min	Gas rate, l/min	Bed temp., °C	Weight loss g (meas.)	Gas analysis chart area, in² (UV transmittance)[b]	Total	$SO_3^=$	$S^=$	$S_2O_3^=$	$SO_4^=$	K_2O	Final wt., g (K_2O balance)[c]	Total sulfur loss	Reduction in sulfite content	Sulfur disproportionation	Sulfide content	Thiosulfate content	Sulfate content	Total S loss as SO_2	Weight loss (K_2O balance)
Raw material analysis									27.5	25.8	0.9	Nil	0.8	42.5									
1	13B	169	S	15	2.5	118	0.3	0.0012	27.6	24.3	0.8	0.1	2.4	42.9	4.9534	0.5722	6.2784	5.7062	-0.3908	0.3602	5.7368	0.3147	0.9324
2	14D	169	S	15	3	107	0.3	0.0016	27.5	24.5	0.6	0.2	2.2	42.9	4.9534	0.9324	5.5580	4.6256	-1.1113	0.7205	5.0163	0.5128	0.9324
3	15B	170	S	30	2.5	123	0.3	0.0089	26.9	22.8	0.9	0.3	2.9	42.8	4.9650	2.8675	11.4902	8.6227	-0.0229	1.0833	7.5624	1.5771	0.7009
4	16B	169	S	30	3	108	0.4	0.0041	27.1	23.2	0.6	0.7	2.6	42.9	4.9534	2.3734	10.2412	7.8678	-1.1113	2.5217	6.4573	1.3054	0.9324
5	2	170	F	15	2.5	146	0.1	0.0330	27.3	23.7	0.4	Nil	3.2	43.3	4.9076	2.5614	9.2286	6.6672	-1.8451	0.0000	8.5123	1.4088	1.8476
6	1	173	F	15	3	151	-0.1	0.0310	27.4	24.5	0.4	Nil	2.5	42.6	4.9883	0.5975	4.9364	4.3389	-1.8216	0.0000	6.1605	0.3286	0.2347
7	4	170	F	30	2.5	147	0.25	0.1210	27.0	23.4	0.6	2.8	0.2	42.7	4.9766	2.2780	9.1256	6.8476	-1.1011	10.1341	-2.1852	1.2529	0.4684
8	3	169	F	30	3	145	0.15	0.1190	27.3	23.2	0.9	0.1	3.1	43.0	4.9419	1.8816	10.4355	8.5539	-0.0381	0.3594	8.2326	1.0349	1.1628
9	10	204	S	15	2.5	143	0.2	0.0640	27.4	22.3	0.9	Nil	4.2	43.0	4.9419	1.5222	13.6702	12.1480	-0.0381	0.0000	12.1860	0.8372	1.1628
10	11	208	S	15	3	138	0.25	0.0230	27.3	22.4	1.0	Nil	3.9	42.8	4.9650	1.4231	12.9346	11.5115	0.3381	0.0000	11.1733	0.7827	0.7009
11	12	207	S	30	2.5	152	0.2	0.4400	26.9	19.1	1.1	0.1	6.6	43.6	4.8739	4.6497	26.1159	21.4662	0.6264	0.3545	20.4854	2.5573	2.5229
12	9	207	S	30	3	137	0.2	0.3800	26.9	17.6	0.9	0.6	7.8	43.5	4.8851	4.4305	31.2894	26.8589	-0.0752	2.1317	24.8025	2.4368	2.2989
13	7	203	F	15	2.5	186	0.05	0.1420	26.9	21.6	0.9	Nil	4.4	43.1	4.9304	3.5436	16.3662	12.8226	-0.0456	0.0000	12.8682	1.9490	1.3921
14	5	206	F	15	3	183	0	0.1560	27.0	21.4	1.3	0.3	4.0	43.6	4.8739	4.2952	17.9633	13.6681	1.3353	1.0634	11.2694	2.3624	2.5229
15	6	207	F	30	2.5	190	0.35	0.7090	25.8	15.2	1.3	0.5	8.8	45.9	4.6296	13.1313	42.6397	29.5084	1.1044	1.6835	26.7205	7.2222	7.4074
16	8	203	F	30	3	182	0.3	0.3360	26.7	18.5	1.3	0.1	6.8	44.4	4.7860	7.0639	29.4242	22.3603	1.2523	0.3481	20.7600	3.8851	4.2793
Average						147.25	0.2031	0.1606						43.3125	4.9078	3.3827	16.1061	12.7234	-0.1840	1.2975	11.6099	1.8605	1.8437
Differences[d] in responses due to																							
Furnace temperature (A)						33.25	-0.019	0.2413						0.850	-0.0943	3.2494	15.3887	12.1393	1.4925	-1.1997	11.8466	1.7872	1.8844
Bed condition (B)						38.00	-0.131	0.0905						0.525	-0.0571	2.0727	2.8177	0.7450	0.0782	0.8021	-0.1352	1.1400	1.1414
Time (C)						1.50	0.131	0.2083						0.575	-0.0628	2.9035	10.4782	7.5747	0.5267	2.0590	4.9890	1.5970	1.2559
Gas rate (D)						-6.75	-0.031	-0.0586						-0.200	0.0211	-1.0160	-1.5166	-0.5005	0.0601	-0.8089	0.2482	-0.5588	-0.4213
Two-factor interactions																							
AB						4.75	0.094	0.0185						0.500	-0.0544	1.9294	2.7782	0.8487	0.6206	-0.6499	0.8780	1.0612	1.0876
AC						1.25	0.006	0.1617						0.650	-0.0713	1.7193	6.6554	4.9362	-0.1971	-1.1954	6.3288	0.9456	1.4266
AD						-1.00	0.019	-0.0564						-0.125	0.0125	-0.3925	-0.2786	0.1139	0.2407	1.1851	-1.3120	-0.2158	-0.2495
BC						-2.00	0.119	0.0225						0.275	-0.0287	0.4357	0.3044	-0.1314	0.3719	0.8064	-1.3098	0.2396	0.5742
BD						4.75	-0.069	-0.0322						-0.150	0.0154	-0.9030	-2.1336	-1.2307	0.5937	-1.7028	-0.1216	-0.4966	-0.3077
CD						-3.25	0.019	-0.0514						-0.100	0.0093	-0.7782	-0.4788	0.2995	-0.2049	-1.1648	1.6692	-0.4280	-0.1853
Least significant differences																							
90% confidence						2.569	0.0570	0.0812						0.5659	0.0613	1.7737	4.3427	2.7991	0.4476	2.5597	4.0176	0.9756	1.2208
95% confidence						3.277	0.0728	0.1036						0.7221	0.0782	2.2631	5.5410	3.5715	0.5711	3.2659	5.1262	1.2447	1.5576
99% confidence						5.140	0.1141	0.1625						1.1324	0.1226	3.5492	8.6898	5.6011	0.8957	5.1218	8.0392	1.9521	2.4428

[a] S = static bed, sweep gas passed through space above bed. F = fluidized bed, sweep gas passed through bed.

[b] Off-gas diluted and passed through 10-cm flow cell in UV analyzer set at 287 nanometers.

[c] Initial weight of $K_2S_2O_5$ was 5.00 grams.

[d] Negative sign indicates increase in response at the higher level of the variable; underlined values are significant at 90% confidence level.

33.25°C and that there is greater than 99% confidence that this is a real effect of the furnace temperature variation. An even more effective variable, however, was the variation in bed condition; the tests with the bed fluidized averaged 38°C hotter than the static bed tests. This probably was due to the transfer of heat into the bed more rapidly with the incoming gas, to the removal of decomposition products (SO_2 and moisture) from the bed, and to the mixing of the bed which exposed more particles to the warmer edges of the bed. There were smaller, but still at least 90% significant, differences due to the gas rate (higher gas rate lowered temperature), and to the interactions of furnace temperature and bed condition (AB) in which the temperature averaged 4.75°C higher when the furnace temperature and bed condition had the same sign (either + or -) than when the signs of these variables were mixed. Also effective were the interactions BD and CD.

Weight loss from the samples was measured to the nearest 0.05 gram. This measurement was not precise enough to give highly significant results and greater than 0.057-gram differences were required for 90% confidence in the effects. Bed condition and time, along with the AB, BC, and BD interactions, were significant. The lack of precision in this measurement was the result of the relatively small sample weight (5 g) and the large weight of the decomposition chamber (about 500 g) in which it had to be weighed. In order to get better material balances, it was decided to calculate the product weight from the input weight and the K_2O analyses of the products and the raw material. Since there should have been no K_2O loss, the weight calculated by this means should be about as accurate as the analytical method, the variation of which should give results within .05% or a variation in product weight of 0.006 gram. The material balances were calculated from the weights determined in this manner.

Measurement of SO_2 in the off-gas stream, as reflected by the area under the UV analyzer curve, responded to variations in temperature, bed condition, and time, along with the temperature-time (AC) interaction. Temperature and time were the most effective of the variables, higher temperature and longer time increasing the amount of SO_2 in the off-gas stream.

Since the remainder of the responses were to be based on the weight calculated from the K_2O analyses, it was decided to determine what effect the variables had on the product K_2O analyses. These values were affected only by the temperature and time variables and their interaction as would be expected. Higher temperatures and longer times caused greater losses of weight and thus increased the K_2O content of the residue. Temperature was the most effective of the variables in these tests.

The final weight, based on K_2O analyses, responded to the same variables and in the same order as did the K_2O analyses but in the reverse direction, as expected.

Loss of total sulfur content averaged about 3.4% of the input sulfur or about 6.8% of that desired in the process. A maximum value of 13.1% (26.2% of desired) was attained. Total sulfur loss was increased by increases in temperature and time, by fluidizing the bed, and by the interaction of temperature and bed condition.

Reduction in sulfite content averaged 16.1% and reached a maximum of 42.6%. A value of 50% is theoretical for pure $K_2S_2O_5$. More sulfite was lost at higher temperatures, longer times, and the interaction between the two.

The proportion of the input sulfur that was changed in oxidation state (disproportionation) was calculated as the difference in total sulfur loss and sulfite sulfur loss. This sulfur was still present but in different states of oxidation. Disproportionation was increased by the same variables that increased the sulfite sulfur loss and in the same order (temperature > time > AC interaction). Of the average 16.1% sulfite sulfur lost, 12.7% (79% of that lost) was due to disproportionation. Reduction of this value is highly desirable but the changing of any of the variables which caused disproportionation would adversely affect sulfite loss which is the purpose of the procedure.

Increases in sulfide, thiosulfate, and sulfate sulfur content were measured to determine the forms to which the sulfite sulfur was altered. Sulfate sulfur was calculated as the difference between the total sulfur content and the sum of the values for the other forms. None of the variables had a significant effect on the thiosulfate sulfur increase which averaged about 1.3% of the input sulfur and varied up to 10.1%. Both the sulfide and sulfate sulfur contents increased with increases in temperature and time. Sulfide sulfur was increased also by the AB and BD interactions while sulfate sulfur was increased by the AC interaction. The primary phase produced during disproportionation was sulfate; the second most abundant was thiosulfate. It is noted, however, that the oxygen requirement for the indicated amounts of sulfate and thiosulfate produced (averages) is greater (about 127%) than the amount of oxygen available from the sulfite disproportionated.

The total weight of the sulfur lost, calculated as SO_2, averaged about 1.86% of the input sample weight. This value compares very favorably with the weight loss of 1.84% as calculated by the K_2O balance. Both these values were increased most by increases in temperature and time although the sulfur loss value was increased by fluidizing the bed also. Interaction AB increased sulfur loss and AC increased weight loss.

It was concluded from this part of the study that temperature was the most significant factor in causing disproportionation and that disproportionation was not decreased by rapid removal of the gaseous decomposition products from the solid residue. The latter was the primary purpose of the tests. Generally, the tests resulted in a reduction in sulfite sulfur equivalent to about five times the value of the total sulfur lost from the sample. Since most of the sulfur lost was probably lost as sulfur dioxide, disproportionation probably accounts for about 80% of the sulfite sulfur reduction. The disproportionation reaction appears to be one in which sulfur dioxide is reproportioned, primarily, to sulfate and thiosulfate.

Further Tests, Effects of P_2O_5 and Moisture

Exploratory tests were made to determine the effects of further increases in furnace temperature, of the addition of phosphate, and of the addition of antioxidants to the system. The latter two test series were made to attain a better understanding of the potassium phosphate system and the use of antioxidants to suppress oxidation in the scrubber system. Tests with P_2O_5 present, added as monopotassium phosphate were promising.

Pertinent data from those tests, along with comparative tests without P_2O_5, are given below. The addition of P_2O_5 decreased the overall reduction in sulfite content while increasing the total sulfur evolution from the samples, thus decreasing significantly the proportion of sulfur disproportioned.

P_2O_5 content, %	Furnace temp., °C	Time, min	Gas rate, l/min[a]	Reduction in sulfite sulfur, % of input S	Total sulfur evolution, % of input S	Sulfur disproportionation, % of input S
Tests with 15-Minute Retention Time						
5	202	15	2.5	12.28	11.27	1.00
5	204	15	2.5	11.46	7.99	3.47
			Average	11.87	9.63	2.24
0	203	15	2.5	16.37	3.54	12.82
			Improvement	4.50	6.09	10.58
Tests with 30-Minute Retention Time						
5	202	30	2.5	27.21	13.99	13.22
5	204	30	2.5	33.91	16.43	17.49
			Average	30.56	15.21	15.36
0	207	30	2.5	42.64	13.13	29.51
			Improvement	12.08	2.08	14.15

[a] In all tests the bed was fluidized.

A second factorial test was planned in which the effects of potassium phosphate addition was the primary area of study. It was possible that, at the temperatures of the test (168° and 204°C) in the exploratory work, some water might have been released as the result of conversion of P_2O_5 to polyphosphate forms and that this water might have inhibited disproportionation. Also, in earlier work (November 1970 Applied Research Branch Progress Report, TVA), it was reported that the use of moist sweep gas gave the lowest sulfate proportion in the product. The new test series was designed, therefore, to determine the effects of time, temperature, P_2O_5 content, and moisture content of the sweep gas on the thermal decomposition of $K_2S_2O_5$.

Variables and levels tested in the present series are indicated in the following tabulation.

Variable	Level	
	-1	+1
Temperature, °C	168	204
Time, min	15	30
P_2O_5 content of feed, %	5	10
Moisture in sweep gas	0[a]	Sat.[b]

[a] Sweep gas, 2.5 l/min dry N_2.

[b] Sweep gas, 2.5 l/min N_2 saturated with water at 25°C.

The decomposition chamber, pot furnace, and sweep gas metering system used in these tests were the same as were used in the earlier series. Changes made in the rest of the system were as follows: (1) the UV cell and dilution gas system were removed, (2) the gas was directed through the fritted disk and sample in all the current tests, and (3) a water-filled gas-absorption bottle, fitted with a fritted sparger, was installed as a saturator between the sweep gas meter and the decomposition chamber for use in the tests where the sweep gas was saturated with water vapor.

Evaluation of Data

Results of these tests and the statistical analyses of the several measured or calculated responses are given in Table 2. Since the addition of phosphate was a new feature of the system, analyses were made of the residue after the tests to determine its retention. A material balance, based on total retention of the K_2O in the sample, indicated an average gain in P_2O_5 of 0.02 gram or about 5% of the average input P_2O_5 content. This value is very small, considering the method used to make the calculations. None of the variables had significant effect on the P_2O_5 retention in the sample so any variation was considered as error.

Total sulfur evolution averaged 10.5% and was increased by increases in temperature, time, moisture content of the sweep gas, and the interactions of temperature with time (AB) and moisture content of the gas (AD). The change in temperature resulted in the greatest difference but the addition of moisture was almost as effective.

Reduction in the sulfite sulfur content averaged 16% and was due to the same three individual variables with temperature being the most effective, time was next, and moisture content the least effective; the temperature-time interaction was significant also.

Disproportionation, the difference between the reduction in sulfite sulfur content and total sulfur evolution, responded to temperature changes only.

The forms of the disproportionated sulfur compounds were determined from analyses for total, sulfite, sulfide, and thiosulfate sulfurs; sulfate sulfur was calculated as the difference between the total sulfur content and the sum of the remaining forms.

TABLE 2. THERMAL DECOMPOSITION OF POTASSIUM METABISULFITE

FACTORIAL TEST 2--DATA AND ANALYSIS

		Test conditions				Responses																		
								Chemical analysis, % by wt.									% of input sulfur						% of input weight	
								Sulfur												Increase in				
Plan position	Test No.	Furnace temp., °C	Time, min	P_2O_5 content, %	Gas moisture content[a]	Bed temp., °C	Weight loss, g (meas.)	Total	$SO_3^=$	$S^=$	$S_2O_3^=$	$SO_4^=$	K_2O	P_2O_5	Final wt., g (K_2O balance)[b]	P_2O_5 loss, g	Total sulfur evolution	Reduction in sulfite content	Sulfur disproportionation	Sulfide content	Thiosulfate content	Sulfate content	Total S evolution as SO_2	Weight loss, (K_2O balance)
1	13	168	15	5	Dry	153	0.15	25.4	21.9	0.1	< 0.1	3.35	42.5	5.5	5.0000	-0.0150	-2.0080	0	2.0080	0.2008	-1.4056	3.2129	-1.0000	0
2	10A				Sat.	154	-0.15	23.8	21.0	< 0.1	0.1	2.65	43.3	5.3	4.9076	-0.0001	6.1836	5.1727	-1.0109	-0.0037	-1.2122	0.2050	3.0794	1.8476
3	11			10	Dry	156	0.20	21.9	19.6	0.2	< 0.1	2.05	41.9	10.6	4.9761	-0.0100	0.9297	-1.8475	-2.7772	0.6775	-1.1374	-2.3172	0.4091	0.4773
4	12A				Sat.	151	0.00	20.8	18.2	< 0.1	0.3	2.25	42.9	11.3	4.8601	-0.0317	8.0992	6.4050	-1.6942	-0.0064	-0.0381	-1.6497	3.5636	2.7972
5	9		30	5	Dry	151	-0.05	24.9	21.4	< 0.1	0.2	3.25	42.6	5.3	4.9883	-0.0044	0.2347	2.2098	1.9751	-0.0005	-0.8051	2.7806	0.1169	0.2347
6	14A				Sat.	151	0.05	23.8	19.9	0.1	0.3	3.50	44.5	5.5	4.7753	-0.0026	8.7135	11.6240	2.9105	0.1828	-0.4558	3.1835	4.3393	4.4944
7	15			10	Dry	153	0.05	21.1	18.9	< 0.1	0.4	1.75	42.2	10.5	4.9408	-0.0013	5.2273	1.9270	-3.3003	-0.0027	0.4330	-3.7306	2.3000	1.1848
8	16A				Sat.	154	0.15	20.9	18.5	< 0.1	< 0.1	2.30	42.8	11.3	4.8715	-0.0330	7.4416	4.8885	-2.5531	-0.0058	-1.1422	-1.4051	3.2743	2.5701
9	3	204	15	5	Dry	187	0.20	24.6	17.8	0.2	0.3	6.30	43.5	6.0	4.8851	-0.0331	3.4760	18.1092	14.6332	0.5839	-0.4293	14.4786	1.7310	2.2989
10	6A				Sat.	186	0.25	22.8	17.1	0.1	0.7	4.90	44.4	5.6	4.7860	-0.0080	12.3521	22.2159	9.8638	0.1836	1.0845	8.5956	6.1514	4.2793
11	8A			10	Dry	189	0.30	20.6	16.7	0.1	0.6	3.20	42.5	12.5	4.9059	-0.0957	8.1262	12.3380	4.2118	0.2187	1.3123	2.6807	3.5755	1.8824
12	4A				Sat.	183	0.05	20.3	14.9	0.1	0.3	5.00	45.0	11.0	4.6333	0.0078	14.4939	24.0576	9.5637	0.1939	-0.1000	9.4697	6.3773	7.3333
13	5		30	5	Dry	184	0.55	23.0	15.8	0.2	1.2	5.80	44.1	5.0	4.8186	0.0191	10.9818	26.8002	15.8184	0.5733	3.0380	12.2071	5.4689	3.6281
14	7				Sat.	184	-0.05	17.7	12.6	0.2	0.7	4.20	46.0	5.1	4.6196	0.0244	34.3243	41.1996	6.8753	0.5413	0.9909	5.3431	17.0935	7.6087
15	1B			10	Dry	188	0.60	20.9	12.8	0.1	1.3	6.70	45.9	12.2	4.5425	-0.0367	13.6928	33.9602	20.2674	0.1857	4.0048	16.0769	6.0248	9.1503
16	2B				Sat.	184	0.60	15.9	10.1	0.1	1.2	4.50	47.4	13.4	4.3987	-0.0719	36.4183	46.4298	10.0115	0.1726	3.4350	6.4039	16.0241	12.0253
Average																-0.0219	10.5429	15.9681	5.4252	0.2309	0.2410	4.7209	4.9081	3.8633
Raw materials																								
I				5				24.9	21.9	< 0.1	0.4	2.55	42.5	5.2										
II				10				22.0	19.1	< 0.1	0.3	2.55	41.7	10.35										
Differences[c] in responses due to																								
Furnace temperature (A)																-0.0047	12.3805	24.3414	11.9609	0.2013	2.8521	9.3721	5.7955	4.3250
Time, min (B)																0.0173	8.1727	10.3235	2.1508	-0.0502	1.8927	0.7729	3.8443	2.4976
P_2O_5 content (C)																-0.0243	2.5213	0.1034	-2.4180	-0.1035	1.2099	-3.0597	0.5710	1.6286
Gas moisture content (D)																0.0004	10.9207	8.5620	-2.3588	-0.1473	-0.7707	-1.9053	5.1596	3.0124
Two-factor interactions																								
AB																-0.0013	6.0695	7.5937	1.5242	0.1234	0.5076	0.4287	2.8497	1.6571
AC																-0.0255	0.3779	2.0118	1.6339	-0.1743	-0.2179	1.5615	-0.1818	1.5154
AD																0.0096	4.4072	2.1118	-2.2954	0.0297	-0.7874	-2.0023	2.0519	0.5593
BC																-0.0206	-0.3899	1.2396	1.6296	-0.1333	-0.2192	1.5175	-0.4199	0.6125
BD																-0.0300	3.2695	1.2491	-2.0204	0.1811	-1.1193	-1.5467	1.5456	0.1127
CD																-0.0113	-1.3015	0.2888	1.5902	-0.0339	-0.7731	1.9327	-0.9271	-0.0046
Least significant differences																								
90% confidence																0.0403	4.1231	3.7501	4.2533	0.1631	0.7925	4.2047	1.9022	1.5336
95% confidence																0.0514	5.2608	4.7849	5.4269	0.2081	1.0112	5.3649	2.4270	1.9568
99% confidence																0.0806	8.2503	7.5040	8.5107	0.3264	1.5858	8.4136	3.8062	3.0688

[a] Saturated gas prepared by passing dry gas through fritted glass plug in gas scrubber bottle filled with water.

[b] Initial weight of charge 5.00 grams.

[c] Negative sign indicates increase in response at the higher level of the variable; underlined values are significant at 90% confidence level.

The sulfide and thiosulfite sulfur contents increased about 0.2% each (average) and the sulfate sulfur content increased about 5%. All three were increased most severely by increasing the furnace temperature. The thiosulfate content was increased also by time and P_2O_5 content. Interaction AC decreased sulfide content while BD increased it. Interaction BD decreased thiosulfate content.

Total sulfur loss (calculated as SO_2), percent of weight, followed the same pattern as total sulfur loss, percent of input sulfur. The weight loss calculated from the K_2O balance reponded to all the individual variables and to the AB interaction. Total sulfur loss, calculated as SO_2, was greater (4.9% vs. 3.9%) than that calculated from the K_2O balance. A linear regression of all the values for sulfur evolution as SO_2 and weight loss gives the following equation with a correlation coefficient of 0.85.

$$\text{Weight loss} = 0.59\ (SO_2\ \text{evolution}) + 1$$

This indicates that the weight loss was not due to the SO_2 evolution only. However, if the regression is made on the results from runs with dry gas only, the equation (correlation coefficient 0.84) becomes:

$$\text{Weight loss} = 0.99\ (SO_2\ \text{evolution}) + 0.05$$

This shows the weight loss to be primarily SO_2 and indicates that the samples from tests in which moisture was added may contain a considerably greater portion of water than those made with dry gas. The moisture addition assisted in SO_2 release but the amount of SO_2 released is not determined by the weight loss from the sample in this case.

The proportion of sulfur disproportionated in this series of tests was 5.4% or 34% of the sulfite sulfur reduction. This value, calculated for the previous series, was 79%. Although increasing the P_2O_5 content from 5 to 10% did not significantly affect disproportionation, the addition of 5% P_2O_5 did have a large depressing effect. Apparently the major part of the improvement was due to the first 5% or less. Lowering disproportionation from 79% to 34% would have a large effect on the amount of material that would have to be processed through a reduction step or would have to be bled from the system.

Conclusions

Although the addition of KH_2PO_4 to the raw material reduced disproportionation and the addition of moisture to the sweep gas increased SO_2 evolution, no combination of conditions tested resulted in elimination of disproportionation. It appears that increased SO_2 evolution might be attained by increasing temperature, time, and maintaining a moist sweep gas; but the production of sulfate, sulfide, and thiosulfate would have to be accommodated. One method under consideration for accomplishing this would be to decompose metabisulfite thermally to the extent that one-third of the sulfur was evolved as SO_2 and then reduce the remaining two-thirds to the sulfide by reaction with a reducing agent. The sulfide then would be converted to hydrogen sulfide by reaction with water and CO_2, producing the carbonate for return to the scrubber and supplying raw materials for the Claus reaction to produce elemental sulfur. Equations for the entire process are shown below.

Scrubber

$$3K_2CO_3 + 6SO_2 \longrightarrow 3K_2S_2O_5 + 3CO_2$$

Decomposition

$$3K_2S_2O_5 \longrightarrow 2SO_2 + 2K_2SO_4 + K_2S_2O_3$$

Reduction

$$2K_2SO_4 + K_2S_2O_3 + K_2CO_3 + 6C \longrightarrow 4K_2S + 7CO_2$$

H_2S production

$$4K_2S + 4H_2O + 4CO_2 \longrightarrow 4K_2CO_3 + 4H_2S$$

Claus reaction

$$4H_2S + 2SO_2 \longrightarrow 4H_2O + 6S^\circ$$

It is presumed that the P_2O_5 would remain with solids through the H_2S production step and then be recycled to the scrubber.

The present results indicate that enough SO_2 could be evolved from potassium metabisulfite by heating to satisfy the needs of the process described by these equations and that a viable process of this nature could be possible.

As a result of these two studies of the thermal decomposition of potassium metabisulfite, it was concluded that sulfur evolution as SO_2 and disproportionation to unwanted forms may be improved by the inclusion of phosphate (added as KH_2PO_4 in these tests) to the solids being decomposed and by the addition of moisture to the sweep gas. Rapid removal of liberated gases from the sample did not affect disproportionation significantly indicating that reaction of liberated SO_2 with the remaining solids probably is not a cause of disproportionation. The other factors (temperature, time, bed condition, and sweep gas flow), when applied so as to increase sulfite loss from the sample, also increased disproportionation.

REDUCTION OF POTASSIUM SULFATE WITH CARBON

Most of the sulfur in the solids, after the scrubbing and thermal decomposition steps, is in the sulfate form. Recovery of the potassium and sulfur values of the material is important for economic reasons. Reduction with carbon at elevated temperatures to yield potassium sulfide and subsequent reaction with water and carbon dioxide would yield the desired products as illustrated by the following equations:

$$K_2SO_4 + C \longrightarrow K_2S + CO_2$$

$$K_2S + 2H_2O \longrightarrow 2KOH + H_2S$$

$$2KOH + CO_2 \longrightarrow K_2CO_3$$

Earlier work (October 1969 and March 1970 Applied Research Branch reports, TVA) with various reducing agents, including coke, on reduction of K_2SO_4 had indicated loss of both K_2O and S from the samples, the production of some unwanted sulfur species ($K_2S_2O_3$ and/or polysulfides), and incomplete reactions. Some of the results apparently were due to reoxidation of the charge on removal from the reduction furnace. Some advances have been made in both analytical and test procedures since the earlier work.

Test Plan and Equipment

The process now has been restudied using a factorial test design in an attempt to determine the effects of four variables at each of two levels on the reduction of reagent-grade K_2SO_4. The variables were temperature, sweep gas rate, time, and carbon proportion. Prior to this series of tests, some work was done to assist in selecting the most suitable of a list of reducing agents and the ranges over which the variables were effective. Reducing agents tested were bituminous coal, graphite, coconut charcoal, and coke breeze. Coke breeze was selected as the most effective and was used in the present tests. Levels of the variables tested are given below. The conditions were chosen to result in less than complete reduction.

Variable	Levels -	Levels +
A - Temperature, °C	815	927
B - Sweep gas flow (N_2), ml/min	25	75
C - Time subjected to test temperature, min	30	60
D - Carbon proportion, %[a]	54	91

[a] % of stoichiometric for the reaction: $K_2SO_4 + 4C \longrightarrow K_2S + 4CO$. Carbon proportion values would be twice as great if based on reaction to form CO_2 instead of CO.

The tests were made in an electrically heated tube furnace lined with a fused silica tube which was restricted on both ends, and through which a flow of nitrogen sweep gas was passed to remove any gaseous reaction products. A rod and packing gland arrangement in one end of the tube (gas discharge end) allowed insertion of a sample into the hot zone of the furnace after purging it with N_2 and withdrawal of the sample from the hot zone to allow cooling in the N_2 atmosphere to below 52°C before exposing the reduced product to air. The method should minimize reoxidation. The apparatus is shown in Figure 4.

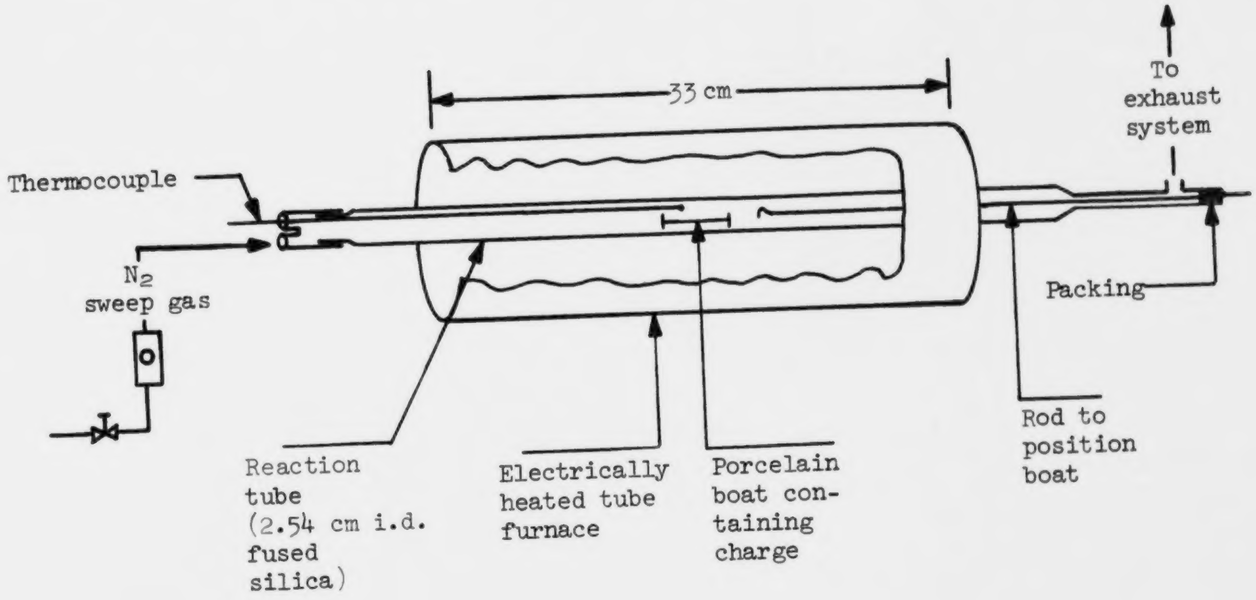

33 cm
To exhaust system
Thermocouple
N$_2$ sweep gas
Packing
Reaction tube (2.54 cm i.d. fused silica)
Electrically heated tube furnace
Porcelain boat containing charge
Rod to position boat

Figure 4. Laboratory apparatus used in tests of the reduction of potassium sulfate with coke breeze.

Evaluation of Data

Losses and gains of chemical species, on which basis the tests were evaluated, were calculated from the weights and analyses of the raw materials and products. Analytical determinations were made of the K_2O, total sulfur, sulfite sulfur, sulfide sulfur, and thiosulfate sulfur. Sulfate sulfur was calculated as the difference between total sulfur and the sum of the other species. Ranges of the losses and gains are listed below.

	Low	High	Average
Losses, % of input			
K_2O	0.66	24.24	9.94
Total S	0	20.07	6.59
Sulfate S	20.59	94.38	55.47
Gains, % of input S			
Sulfite S	5.53	20.92	11.14
Sulfide S	4.70	54.44	32.69
Thiosulfate S	1.26	15.87	5.05

The aim of the process is to achieve essentially complete reduction of sulfate sulfur to sulfide form. Sulfite sulfur results from incomplete reduction. Thiosulfate results from disproportionation or a reaction of sulfite with elemental sulfur or a polysulfide. Losses of K_2O and total S result from volatilization or from spatter. The K_2O:S mole ratio in the materials lost from the samples averaged about 1.4.

Results of the current tests are given in Table 3 in which are shown the conditions, product weights, product analyses, and indices calculated from the product weights and analyses. Of the statistical analysis, the differences in responses for the individual variables and the two factor interactions are shown, along with the minimum differences for which there is 90, 95, and 99% confidence in the reality of the effect. The differences in which there is at least 90% confidence are underlined. The three- and four-factor interactions were considered as error in these calculations.

The potassium sulfate used in the tests was reagent-grade material; the coke breeze contained 72.6% carbon. Responses on which the evaluation was made were calculated from material balances based on the chemical analysis and weights of the input materials and the residue.

The loss of K_2O is a physical loss from the sample due to volatilization or to spatter. It responded to all the individual variables, being greater at the more severe condition, and to all the two-factor interactions except that of time-carbon proportion. Average loss of K_2O amounted to about 10% of the input. Conditions causing greatest losses were furnace temperature, carbon proportion, and the interaction of the two. Conditions that restricted the loss were all the interactions involving nitrogen flow.

TABLE 3. REDUCTION OF POTASSIUM SULFATE WITH COKE BREEZE[a] (LABORATORY TESTS)

FACTORIAL TEST--DATA AND ANALYSIS

		Test conditions				Responses													
						Weight, g		Chemical analysis, % by wt.						Loss, % of input		% of input total sulfur			
								Sulfur								Loss	Gain		
Plan position	Test No.	Furnace temp., °C	N_2 flow, ml/min	Time, min	Carbon proportion[b]	Input	Residue	Total	$SO_3^=$	$S^=$	$S_2O_3^=$	$SO_4^=$	K_2O	K_2O	Sulfur	$SO_4^=$	$SO_3^=$	$S^=$	$S_2O_3^=$
1	1	815	25	30	0.54	6.034	5.4125[c]	17.0	0.6	2.1	0.8	13.5	49.6	0.659	0.000	20.59	3.53	12.35	4.71
2	4	815	25	30	0.91	6.723	5.8297	15.1	1.0	2.8	1.0	10.3	44.7	3.573	4.329	34.74	6.34	17.74	6.34
3	5	815	25	60	0.54	6.034	5.0210	18.0	1.1	4.0	0.8	12.1	52.6	2.272	1.776	33.97	6.00	21.83	4.37
4	6	815	25	60	0.91	6.723	5.0630	17.5	1.7	7.0	0.6	8.2	51.1	4.263	3.706	54.88	9.35	38.52	3.30
5	7	815	75	30	0.54	6.034	5.4085	16.2	0.3	0.8	2.7	12.4	46.9	6.235	4.776	27.11	1.76	4.70	15.87
6	8	815	75	30	0.91	6.723	5.7952	15.5	0.7	3.0	0.2	11.6	44.0	5.643	2.377	26.94	4.41	18.89	1.26
7	2	815	75	60	0.54	6.034	5.0060	17.8	1.0	4.0	0.5	12.3	51.0	5.528	3.158	33.08	5.44	21.76	2.72
8	3	815	75	60	0.91	6.723	5.1102	17.6	2.0	6.2	0.5	8.9	50.3	4.883	2.252	50.57	11.11	34.43	2.78
9	16	927	25	30	0.54	6.034	4.4115	19.7	2.1	7.3	0.7	9.6	57.2	6.626	5.549	53.97	10.07	35.00	3.36
10	13	927	25	30	0.91	6.723	4.2221	19.0	4.5	10.5	2.2	1.8	52.3	18.288	12.816	91.74	20.65	48.18	10.09
11	9	927	25	60	0.54	6.034	4.0310	20.9	3.0	9.1	0.6	8.2	59.0	11.993	8.438	64.08	13.14	39.87	2.63
12	10A	927	25	60	0.91	6.723	3.9754	18.5	3.6	12.6	1.0	1.3	51.5	24.241	20.071	94.38	15.55	54.44	4.32
13	15	927	75	30	0.54	6.034	4.3415	19.9	2.0	7.6	0.4	9.9	57.0	8.428	6.103	53.29	9.44	35.86	1.89
14	14	927	75	30	0.91	6.723	4.2137	18.8	4.3	10.2	2.6	1.7	51.9	19.076	13.907	92.21	19.69	46.71	11.91
15	12	927	75	60	0.54	6.034	3.9598	21.0	3.0	9.2	0.7	8.1	58.2	14.722	9.627	65.14	12.91	39.59	3.01
16	11	927	75	60	0.91	6.723	4.0104	19.6	4.8	12.2	0.5	2.1	52.2	22.537	14.572	90.85	20.92	53.17	2.18
Average														9.935	7.091	55.47	10.64	32.69	5.05
Raw materials																			
I Reagent-grade K_2SO_4, 5.000 g																			
II Coke breeze, 1.034 or 1.723 g																			
Differences[d] in responses due to																			
Furnace temperature (A)														11.607	8.589	40.473	9.304	22.825	-0.245
Nitrogen flow (B)														1.892	0.011	-1.145	0.131	-1.603	0.313
Time (C)														2.739	1.718	10.795	2.316	10.523	-3.765
Carbon proportion (D)														5.755	4.325	23.135	5.716	12.640	0.453
Two-factor interactions																			
AB														-0.988	-0.677	0.475	0.756	1.063	-0.665
AC														2.530	1.865	-4.985	-1.649	-5.193	-0.013
AD														4.838	3.587	10.040	2.096	0.405	3.950
BC														-0.667	-1.106	-0.773	1.454	0.175	-1.295
BD														-1.449	-1.964	-2.648	0.929	0.183	-1.793
CD														-0.403	-0.075	0.468	-0.856	1.738	-0.490
Least significant differences																			
90% confidence														0.6357	1.4316	5.6823	1.9208	2.3647	4.6946
95% confidence														0.8112	1.8266	7.2502	2.4508	3.0172	5.9900
99% confidence														1.2721	2.8645	11.3702	3.8435	4.7318	9.3940

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[a] Coke breeze contained only 72.6% carbon; 1.034 g required for 0.54 stoichiometry, 1.723 g for 0.91 stoichiometry.

[b] Fraction of carbon required to satisfy $K_2SO_4 + 4C \longrightarrow K_2S + 4CO$.

[c] Calculated on total sulfur balance to prevent indicated sulfur gain.

[d] Negative sign indicates increase in response at the higher level of the variable; underlined values are significant at 90% confidence level.

Loss of sulfur is a physical loss from the system also. This loss averaged about 7% of the input sulfur. Losses were increased by increases in temperature, carbon proportion, time, and the interaction of temperature with the other two. The carbon proportion-time interaction produced negative results.

The loss of both K_2O and S were increased by increasing the three factors most likely to result in the production of the sulfide (temperature, time, carbon proportion). This could logically indicate the loss as the sulfide (K_2S) which melts at 840°C and is known to be volatilized in some reduction processes as is discussed later. The K_2O:S mole ratio in materials lost was 1.37 indicating a higher loss of potassium than would be accounted for as potassium sulfide.

Loss of sulfate sulfur is desired, especially if the sulfur is retained in sulfide form. Retention in sulfite form is not harmful since the sulfite would be returned to the scrubber where it would form a useful absorbent for sulfur dioxide. The desirability of retention of sulfur in thiosulfate form is questionable; however, it may serve to inhibit oxidation in the scrubber. Loss of sulfate responded, in a positive manner, to all the individual variables except nitrogen flow; it responded positively also to the temperature-carbon proportion interaction.

Gain of sulfite sulfur in the product is the result of incomplete reduction of sulfate. Sulfite formation increased with all the individual variables except nitrogen flow and with the two-factor interaction temperature-carbon proportion. Further increase in the severity of the test conditions except nitrogen flow should eventually result in a decrease in sulfite content because of reduction to sulfide.

The increase in sulfide sulfur is the measure of the degree of completion of the desired reaction. Sulfide sulfur was increased by increasing temperature, time, and carbon proportion. Sulfide sulfur content was decreased by the interaction of temperature and time.

Thiosulfate analyses were so scattered that none of the responses were significant at the 90% confidence level. There was some indication that the proportion of sulfur in this form was decreased by increasing time and increased by the temperature-carbon proportion interaction.

In the visualized process, the potassium sulfide product from the reduction step would be dissolved in water and then carbonated to produce potassium carbonate for recirculation to the scrubber and hydrogen sulfide (H_2S) for feed to a Claus sulfur production unit, along with sulfur dioxide from thermal decompostion of potassium metabisulfite formed in the sulfur dioxide scrubbing step. The K_2O and S volatilized in the reduction step may be recovered if the off-gas from the reduction step is used to carbonate the potassium sulfide solution; the volatilized material would be absorbed and any potassium and sulfur it contained would thus be returned to the system. Any additional required recovery might be accomplished in the stack gas scrubber to which the off-gases from the Claus unit could be fed.

In the event that prevention or reduction of volatilization of K_2O and S becomes desirable, however, techniques might be used that are reported in an Indian publication (3) which claims the addition of excess reducing agents, sand, and magnesium oxide (MgO) to schoenite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) for that purpose. It may be possible to add sand in the envisioned process during the reduction step; the sand could be removed following the hydration-carbonation step. A settling or filtration step would be required and the sand recovered could be recycled to the reduction step, along with any unutilized solid reductants. The addition of MgO would present some different problems due to the solubility of its various salts in the several steps of the process. It might be advantageous to add other forms of SiO_2 or to add P_2O_5. The determination of the effects of any of these additives will require continued testing.

Conclusions

It was concluded from the present tests that potassium sulfate can be reduced effectively by heating it in contact with coke breeze. Some volatilization of both K_2O and S occurs; this is undesirable but may be accommodated since off-gas from the reduction step would be used as a source of CO_2 for the H_2S production step, and the K_2O and S should therefore be recovered along with the CO_2. It appears that the optimization of the process as related to the four variables studied herein will involve increasing temperature, time, and carbon proportion while decreasing or eliminating the nitrogen flow. Increasing time, particularly, should increase sulfide formation. It also appears that reduction of nitrogen flow would help to minimize the imbalance in K_2O and S losses.

Sodium sulfate is reduced by a similar method in the kraft paper process and in a pollution control process developed by Rockwell International. It appears that the potassium sulfate reduction step could be developed also.

SCRUBBING WITH POTASSIUM CARBONATE SOLUTION

A factorial study was made of the effects of four variables at each of two levels on scrubbing efficiency and oxidation during laboratory tests of scrubbing synthetic stack gas with potassium carbonate solution. The variables were (1) potassium concentration, (2) oxygen content of the gas, (3) P_2O_5 presence in the scrubbing solution, and (4) antioxidant presence in the scrubbing solution. The amount of P_2O_5 added was equivalent to about 10% of the total weight of potassium metabisulfate that could be produced from all the potassium present when the solution contained 1% potassium carbonate or 5% when 2% potassium carbonate solution was used.

Test Plan and Equipment

The tests were made in specially designed gas-absorption bottles each of which consisted of a cylindrical section of 32-millimeter glass tubing, flat-bottomed and 13 centimeters deep, and containing a 5-millimeter glass thermocouple shield fused in the side so as to read the temperature about 4 centimeters from the bottom; an enlarged glass section, 75 millimeters in diameter and 75 millimeters high was fused to the top of the previously described section to act as a foam breaker. The top of the foam breaker was reduced and fused to a 29/42 ground glass joint to allow closure, entry of the inlet gas sparger, and directed flow of the exit gas. One scrubber was used per test; it contained 100 milliliters of the scrubbing solution which filled the 32-millimeter cylindrical section of the unit. A small magnetic stir bar in the bottom of the unit served to ensure agitation.

A mixture of synthetic stack gas (3400 ppm SO_2, 19.4% CO_2, balance N_2) and air (either 2 or 5% O_2 in mixture) was sparged into potassium carbonate solution at approximately 1.5 liters per minute through medium porosity fritted glass plug spargers (12-mm-dia and 24-mm-long) mounted so as to clear the stir bars by about 5 millimeters. The actual gas flow was 1440 milliliters per minute of synthetic stack gas with enough air added to obtain the desired oxygen content. A water bath served to maintain the scrubber temperature at 52°C. Off-gases from the scrubber were passed through a water-cooled condenser and a UV spectrophotometer (set at 287 nm) to monitor their sulfur dioxide contents. The tests were terminated when the sulfur dioxide content of the off-gas reached 1500 ppm. A factorial test plan (four variables at two levels each) was designed for this study; it is outlined below.

	Level	
Variable	-	+
A - K_2CO_3 solution concentration, %	1	2
B - O_2:SO_2 mole ratio	6.67	16.67
C - P_2O_5 content, % ($K_{1.5}H_{1.5}PO_4$)	0	0.183
D - Antioxidant (*p*-phenylenediamine) content, %	0	0.1

The plan requires 16 tests; an additional four tests (two additional replicates of the tests with all variables at the negative level and two with all variables at the positive level) were made as a check of the reproducibility of the tests. Problems with reproducibility had hampered completion of an earlier test series of this nature.

Problems in Earlier Tests

During initiation of the current test series, special effort was placed on discovering the reasons for lack of reproducibility in the earlier tests. That earlier experience had resulted in wide variations in the scrubbing time, the degree of oxidation, and the final solution pH in duplicate tests. Special care was taken with solution makeup, equipment cleaning, and test procedure; also, weaker scrubbing solutions were prepared to shorten test times and eliminate the need for excessive makeup of the synthetic stack gas. In addition, a gas chromatograph, not available during the earlier tests, was used to monitor the oxygen content of the scrubber inlet and outlet gases. It was the gas chromatograph that allowed isolation of at least a major cause of the inconsistency of the earlier test results. It was found that back pressure in the inlet gas system increased as the tests proceeded, due to partial plugging of the fritted glass spargers with products of the reaction. The meters used to measure the flows of synthetic stack gas and of air were fitted with ground glass joints to allow easy removal for cleaning or replacement, and when the back pressure in the system became sufficient, the ground glass joint on one or the other of the meters would be forced open (even though they were mounted under some spring pressure); this allowed part of one of the gas components to escape. The small flows and very small movement required to allow the leaks had made detection of such leaks difficult. Rapid oxygen analysis, made possible by the gas chromatograph, allowed determination of sudden changes in oxygen content and helped to pinpoint the leaks. The chromatograph was used throughout the current series of tests, special attention was directed to the meter joints, and small amounts of water were added to the inlet gas as required to flush the fritted plug of reaction products; these precautions improved reproducibility. A table to show reproducibility will be presented later in the report.

Evaluation of Data

Responses measured during the current tests were (1) scrubbing time before 1500 ppm breakthrough, (2) pH of the final scrubbing solution, and (3) chemical analysis of the final scrubbing solution. From the chemical analyses, the total and sulfite sulfur contents, the degree of oxidation, and the degree of reaction [S:K and (S + P):K mole ratios] were calculated. Sulfite analyses were made immediately after each test was completed to prevent errors due to continued oxidation; other analyses were made later.

On receipt of the chemical analyses for total sulfur, P_2O_5, and K_2O, it was found that there was a very wide variation between the total sulfur values reported and those expected, especially in samples from tests containing antioxidant. In the samples from tests with antioxidant, the total sulfur often was less than half the value for sulfite sulfur determined earlier; total sulfur values for samples without antioxidant appeared fairly reasonable. Total sulfur was determined by oxidation and subsequent precipitation of sulfur with barium, and no interference due to the antioxidant was previously known. Values for K_2O and P_2O_5 were as expected.

Since chemical analyses for total sulfur were not reliable (sulfite sulfur had been analyzed immediately on conclusion of the tests and was considered reliable), some other means of deriving the total sulfur value was needed. The total sulfur in the samples should be the total amount fed in the inlet gas less the amount lost in the exit gas. Oxidation in the inlet gas should be essentially zero. Thus the total sulfur could be calculated using the proportional areas of the curves from the recorder of the UV analyzer, which was used as a continuous monitor of the exit gas sulfur dioxide content. The curves were integrated and the total sulfur values determined for each test; these are the values used in this report.

Reproducibility and Accuracy--

Responses from the replicate tests to determine reproducibility are given in Table 4. Values of time required to reach the point of 1500 ppm sulfur dioxide in the exit gas, of final solution pH, of total and sulfite sulfur contents, or proportion of sulfur oxidized, and of the sulfur to potassium mole ratio in the final solution were obtained. Reproducibility was then determined by calculating the standard deviation (n-1 degrees of freedom), the

TABLE 4. REMOVAL OF SULFUR DIOXIDE FROM SYNTHETIC STACK GAS BY POTASSIUM SCRUBBING--REPRODUCIBILITY TESTS

Test position	Variable level	Item	Response					
			Time, min, to 1500 ppm	Final pH	Sulfur, g		% S oxidation	S:K mole ratio
					Total	Sulfite		
1	All (-)	Replicate 1	50.75	3.6	0.3226	0.1068	66.9	0.6688
		Replicate 2	50.5	3.6	0.3092	0.1131	63.4	0.6525
		Replicate 3	47.5	3.4	0.2879	0.0783	72.8	0.6054
		Standard deviation[a]	1.809	0.115	0.0175	0.0185	4.75	0.0329
		Mean	49.583	3.533	0.3066	0.0994	67.70	0.6422
		Error of mean	1.044	0.066	0.0101	0.0107	2.743	0.0190
		Standard % error[b]	3.64	3.26	5.71	18.65	7.01	5.13
2	All (+)	Replicate 1	153.5	4.8	1.0563	0.9235	12.6	0.9825
		Replicate 2	163.25	4.6	1.1328	0.8890	21.5	1.0519
		Replicate 3	153.75	4.6	1.0702	0.8947	16.4	1.0195
		Standard deviation[a]	5.558	0.115	0.0408	0.0184	4.47	0.0347
		Mean	156.833	4.666	1.0864	0.9024	16.83	1.0180
		Error of mean	3.209	0.066	0.0235	0.0106	2.578	0.020
		Standard % error[b]	3.54	2.47	3.75	2.03	2.65	3.41

[a] Based on n-1 degrees of freedom.
[b] Standard deviation, % of mean.

mean, and the error of the mean. Then, to describe the variability as a single value, the standard percent error expressed as standard deviation, percent of the mean was calculated.

Reproducibility in the tests as shown in Table 4 was fairly good, particularly at the (+) variable levels. In tests where all variables were held at the (-) level, variability (standard % error) ranged from 1.9 to 18.7%. Greatest variability occurred in the sulfite sulfur content; the sulfite sulfur content was very small and a variation of only 0.0348 gram of sulfur accounted for the large value. The proportion of total sulfur oxidized varied 7%, largely due to the variation in sulfite sulfur values. The remaining variability values were less than 6%.

In tests where all variables were held at the (+) level, variability ranged only from 2.0 to 4.4%. Values for sulfite sulfur in these tests averaged about nine times as great as in the tests with all variables held at the (-) level.

Accuracy of solution makeup for the tests was indicated by chemical analyses of the spent liquor for K_2O and P_2O_5 content. These results and their variability are given below. Maximum variability was 0.48%; that occurred in the P_2O_5 content and was the result of a single measurement. Apparently there was no problem in solution preparation.

	K_2O content of spent liquor, %				P_2O_5 content of spent liquor, %
	1% K_2CO_3		2% K_2CO_3		
Item	Alone	+ P_2O_5	Alone	+ P_2O_5	
Replicates					
1	0.7025	0.8825	1.4000	1.5825	0.1825
2	0.7000	0.8800	1.3925	1.5800	0.1825
3	0.6975	0.877	1.4050	1.5825	0.1825
4	0.6975	0.8825	1.3950	1.5700	0.1825
5	-	-	-	-	0.1850
6	-	-	-	-	0.1825
7	-	-	-	-	0.1825
8	-	-	-	-	0.1825
Standard deviation[a]	0.0024	0.0024	0.0055	0.0060	0.0009
Mean	0.6994	0.8806	1.3981	1.5788	0.1828
Error of mean	0.0012	0.0012	0.0028	0.0030	0.0003
Standard % error[b]	0.34	0.27	0.40	0.38	0.48

a. Based on n-1 degrees of freedom.
b. Standard deviation, % of mean.

Analysis of Factorial Design--

The mean values for the replicated tests were used in the statistical analysis of the data from the test series. All three- and four-factor interactions (a total of five values) were considered as error in these calculations. From these error values the least significant differences, at the 90, 95, and 99% confidence level, were calculated for the responses due to the levels of each variable and the two-factor interactions of the variables.

The test design, test results, and statistical analysis are given in Table 5. Although the degree of oxidation of the sulfur and degree of reaction of the potassium with sulfur, particularly in sulfite form, are the most important responses in relation to later process steps, other responses were measured also; these included the time required to neutralize the scrubber solution to the point that the off-gas contained 1500 ppm sulfur dioxide, the pH of the final solution, the potassium (K_2O) content of the final solution, and the phosphate (P_2O_5) content of the final solution. Some of these measurements (K_2O and P_2O_5 content) served only to check the accuracy of the test conditions.

The time of the tests was measured and was found to be most significantly affected by two individual factors and their interaction. These factors were the amount of potassium carbonate in the solution and the presence of 0.1% antioxidant. Increasing the potassium carbonate proportion from 1 to 2% of the solution increased the test time by 58 minutes (67-125 min). A similar increase in time (53 min) resulted from the addition of the antioxidant. Increasing the oxygen to sulfur dioxide ratio reduced test time about 3.8 minutes and the presence of P_2O_5 increased test time about 3.4 minutes. The interaction of potassium carbonate content and P_2O_5 presence reduced test time about 3.1 minutes at the higher levels. In these tests, increased time generally results in increased total sulfur removal and increased K_2O reaction within each potassium carbonate concentration level. The improved performance with the addition of the antioxidant is the most significant of these results.

The final pH of the solution was lower than the input and was a function both of increased sulfur dioxide absorption and of oxidation. Values for pH ranged from 4.8 to 3.2. The statistical analysis showed the presence of the antioxidant to be the most effective variable; it resulted in the final pH value being about 1.1 pH points above that of samples without the antioxidant. Higher potassium carbonate content resulted in slightly higher final pH. Increased oxygen content decreased pH, probably because of increased oxidation.

A linear regression was made of the values of pH and of percent oxidation; the equation derived (0.938 correlation coefficient) was

$$\text{pH} = 4.625 - 0.0148\ (\%\ \text{oxidation})$$

This calculation shows the variation of pH to be almost totally dependent on the degree of oxidation of the sulfur ions. The sulfate ion is much more acidic than the sulfite ion.

The total sulfur content of the final scrubber solution responded significantly and positively to all the individual variables. It was significant to all two-factor interactions of the potassium carbonate content, also. The interactions with oxygen proportion and with antioxidant presence were positive; the interaction with P_2O_5 content was negative. Greatest variations (0.35 and 0.39 g) were due to the presence of antioxidant and to potassium carbonate content, respectively. The improvement due to the presence of the antioxidant is the most important of these effects, especially since the doubling in total sulfur content due to potassium carbonate content (0.44 g at 1% and 0.83 g at 2% K_2CO_3) would be expected.

TABLE 5. REMOVAL OF SULFUR DIOXIDE FROM SYNTHETIC STACK GAS BY POTASSIUM SCRUBBING (LABORATORY TESTS)

FACTORIAL TEST--DATA AND ANALYSIS

		Test conditions				Responses									
								Chemical analysis of final solution, g							
										Sulfur				Mole ratios	
Plan position	Test No.	K_2CO_3 content, %	$O_2:SO_2$ mole ratio	P_2O_5 content, %	Antioxidant content, %	Time, min before 1500 ppm breakthrough	pH of final solution	K_2O	P_2O_5	Total[a]	Sulfite	Sulfate	Oxidation, % of sulfur in sulfate form	Total S:K	(Total S + P):K
1	2A,10,10A[b]	1	6.67	0	0	49.58	3.53	0.7025	-	0.3066	0.0994	0.2072	67.6	0.6424	0.6424
2	9	1	6.67	0	0.1	83.6	4.2	0.7000	-	0.5153	0.4691	0.0462	9.0	1.0835	1.0835
3	3A	1	6.67	0.183	0	53.5	3.65	0.8825	0.1825	0.3302	0.1941	0.1361	41.2	0.5507	0.6879
4	1A	1	6.67	0.183	0.1	92.5	4.35	0.8800	0.1825	0.5679	0.4955	0.0724	12.7	0.9499	1.0877
5	11	1	16.67	0	0	43.0	3.2	0.6975	-	0.2922	0.0375	0.2547	87.2	0.6166	0.6166
6	15	1	16.67	0	0.1	80.3	4.3	0.6975	-	0.5549	0.4812	0.0737	13.3	1.1710	1.1710
7	20	1	16.67	0.183	0	49.5	3.2	0.8775	0.1825	0.3378	0.0395	0.2983	88.3	0.5666	0.7046
8	16	1	16.67	0.183	0.1	87.25	4.45	0.8825	0.1825	0.6032	0.5023	0.1000	16.7	1.0060	1.1432
9	6A	2	6.67	0	0	91.75	3.8	1.4000	-	0.5850	0.1389	0.4461	76.3	0.6150	0.6150
10	7A	2	6.67	0	0.1	160.2	4.6	1.3925	-	1.0148	0.9291	0.0857	8.4	1.0726	1.0726
11	4B	2	6.67	0.183	0	90.5	3.4	1.5825	0.1850	0.5581	0.0581	0.5000	89.6	0.5191	0.5966
12	5A	2	6.67	0.183	0.1	165.1	4.8	1.5800	0.1825	1.0339	0.9473	0.0866	8.4	0.9631	1.0398
13	18	2	16.67	0	0	91.0	3.2	1.4050	-	0.6337	0.0145	0.6192	97.7	0.6639	0.6639
14	17	2	16.67	0	0.1	158.5	4.6	1.3950	-	1.0960	0.8825	0.2135	19.5	1.1564	1.1564
15	13	2	16.67	0.183	0	90.3	3.4	1.5825	0.1825	0.6304	0.0902	0.5402	85.7	0.5863	0.6628
16	12,14,19[b]	2	16.67	0.183	0.1	156.83	4.66	1.5700	0.1825	1.0864	0.9024	0.1840	16.9	1.0185	1.0956
Average						96.4631	3.9588			0.6342	0.3926	0.2415	46.1563	0.8239	0.8775
Differences[c] in responses due to															
K_2CO_3 content (A)						58.1187	0.1975			0.3913	0.2056	0.1858	8.3125	0.0011	-0.0293
$O_2:SO_2$ mole ratio (B)						-3.7563	-0.1650			0.0403	-0.0476	0.0880	14.0125	0.0487	0.0486
P_2O_5 content (C)						3.4437	0.0600			0.0187	0.0222	-0.0036	-2.4375	-0.1077	-0.0004
Antioxidant content (D)						53.1437	1.0725			0.3498	0.6172	-0.2674	-66.0875	0.4575	0.4575
Two-factor interactions															
AB						1.0263	-0.0200			0.0233	0.0018	0.0218	-4.7375	0.0152	0.0151
AC						-3.1237	-0.0450			-0.0239	-0.0139	-0.0098	2.1125	0.0025	-0.0279
AD						16.1263	0.1425			0.1061	0.2228	-0.1164	-7.9375	0.0009	-0.0010
BC						-0.6737	0.0425			0.0015	0.0076	-0.0060	-0.0875	0.0001	0.0000
BD						-0.8737	0.1800			0.0118	0.0296	-0.0178	-7.0375	0.0221	0.0221
CD						1.3263	0.0800			0.0089	-0.0008	0.0096	3.5625	-0.0289	-0.0289
Least significant differences															
90% confidence						1.9795	0.1514			0.0142	0.0494	0.450	11.592	0.0226	0.0226
95% confidence						2.5258	0.1933			0.0181	0.0630	0.0574	14.790	0.0288	0.0288
99% confidence						3.9611	0.3032			0.0284	0.0988	0.0900	23.195	0.0452	0.0452

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[a] Values calculated from feed rates, time, and integration of exit gas analysis curves.
[b] Values are averages of three tests.
[c] Negative sign indicates increase in response at the higher level of the variable; underlined values are significant at 90% confidence level.

Sulfite sulfur content responded in a positive direction to potassium carbonate content, antioxidant presence, and to the interaction of these two. By far the greatest improvement was due to the presence of the antioxidant (0.70 vs. 0.08 g). Doubling the potassium carbonate content did not double the sulfite sulfur content (0.29 vs. 0.50 g) probably due to the greater test length and therefore greater opportunity for oxidation in tests with larger amounts of potassium carbonate.

Sulfate sulfur was calculated as the difference between the total and sulfite sulfur values. The amount of sulfate sulfur present varied with changes in potassium carbonate content, antioxidant presence, and the interaction of the two. Oxygen proportion also was an effective variable. Increased potassium carbonate and oxygen content increased the amount of sulfur in sulfate form while the presence of the antioxidant and its interaction with the potassium carbonate content decreased the amount of sulfate sulfur.

The percent sulfur dioxide oxidation is one of the most important of the responses measured. Thermal stripping of sulfur dioxide from fluid scrubber discharge, precipitation of potassium metabisulfite ($K_2S_2O_5$) for later thermal decomposition, or reaction of the scrubber discharge with limestone in a double-alkali process would all be hampered by increased oxidation. The statistical analysis showed that the proportion of sulfur oxidized to sulfate form responded, primarily, to one variable, the presence of the antioxidant. There was a 66 percentage point reduction in oxidation (79% to 13%) due to the presence of the antioxidant. Increasing the proportion of oxygen in the gas increased oxidation by 14%.

The total sulfur to potassium mole ratio was calculated to determine the degree of reaction of sulfur dioxide and potassium carbonate. The proportion of oxygen, the presence of P_2O_5, and the presence of the antioxidant were significant. Oxygen and antioxidant responses were positive; P_2O_5 presence gave a negative response, probably due to the increase in K_2O content when P_2O_5 was present (added as $K_{1.5}H_{1.5}PO_4$). The interaction of P_2O_5 and antioxidant presence was significant and was negative. The most effective variable was the presence of antioxidant. The reason for increased oxygen content to cause an increase in the sulfur to potassium ratio is not immediately apparent.

The total sulfur-plus-phosphorus to potassium mole ratio was calculated to remove, to some extent, the effect of the increased potassium content when P_2O_5 was present. Results were significant and positive for variations in oxygen proportion and antioxidant presence. Potassium carbonate concentration and the P_2O_5 antioxidant interaction were significant and negative. This ratio almost entirely eliminated the effect of the P_2O_5 presence and probably means that, in effect, the potassium phosphate in the product is in the form of dissolved monopotassium phosphate (KH_2PO_4). In all probability, the addition of P_2O_5 as a 1:1 molar mixture of monopotassium and dipotassium phosphate ($K_{1.5}H_{1.5}PO_4$) increased the scrubbing potential slightly. This was shown in the increased total sulfur content of 0.0187 gram because of the presence of P_2O_5; it is noted that the increase in sulfite sulfur was not significant because of this variable.

Conclusions

It is concluded from this work that the inclusion of an antioxidant in potassium carbonate scrubbing solution results in significant improvement in the process by reducing oxidation and increasing total sulfur and sulfite sulfur absorption. The antioxidant probably would be destroyed in the reduction step, but the concentration reaching this step should be extremely low because of very low concentration in the scrubber solution. The addition of P_2O_5 as potassium phosphate increased total sulfur content by providing some additional scrubbing cation but otherwise did not affect the scrubbing process significantly. Increasing the oxygen content of the input gas from an oxygen to sulfur dioxide mole ratio of 6.67 to 16.67 (O_2 content variation from 2-5%) affected the proportion of sulfur oxidized only slightly.

OXIDATION OF SULFITES

PRIOR WORK

A few laboratory-scale tests had been made earlier (August 1970, August 1972, and October 1972 Applied Research Branch Reports, TVA) using a spinning cup patterned after a device developed and patented in Japan (4). Some of these tests had shown that weak solutions (about 1%) could be oxidized almost completely with about 40 times stoichiometric air; stronger solutions were not tested. Oxidation of slurries of sulfites having lower solubility ($ZnSO_3$) proceeded somewhat more slowly. Oxidation of slurries of calcium sulfite proceeded very slowly unless the pH of the slurry was lowered to increase the solubility of the sulfite. Oxidation of calcium sulfite was shown to be catalyzed by the presence of iron compounds. All the above work was done with the spinning cup model operating in a glass vessel as described in the equipment section of this report.

EQUIPMENT AND PROCEDURE

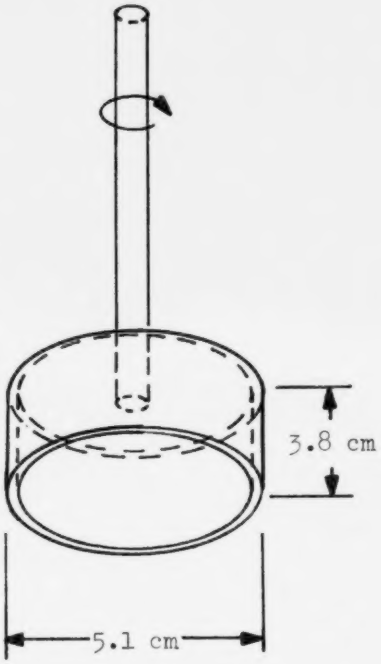
The equipment used in the work included two rotary devices to disperse air into a pool of liquid, a variable speed motor with torque measuring controller to drive these devices, and a series of five tanks in which the oxidation reaction occurred. Aside from the various support stands, thermometer clamps, and so forth required, various scrubbers were used to measure the amounts of ammonia and SO_2 in the off-gases or to dry the off-gas prior to injection of samples into a gas chromatograph set up to measure the O_2:N_2 ratio and thus determine oxygen utilization.

Figures 5 through 7 show the various oxidizers and oxidizing vessels. The spinning cup, as noted earlier, is a model of a similar device patented in Japan; this model was constructed from a description of the unit furnished by A. V. Slack (formerly Chief, Applied Research Branch, Division of Chemical Development, TVA; currently president of SAS, a consulting firm) on his return from a visit to sulfur dioxide control facilities in Asia in 1970. The centrifugal gas-liquor contactor was designed and constructed at TVA and was later found to be similar to but more simply constructed and operated than a mixer patented by Max L. Bard (5).

In operation, the fluid to be oxidized was placed in the oxidizing tank and the oxidizer unit and air inlet tube were immersed to the predetermined depths and the unit was rotated slowly as the fluid temperature was brought to the desired level (52°C). Once the temperature was attained, the unit rpm was adjusted to that desired for the test, and the proper amount of air (4120 ml/min as measured by rotameter) was directed into the unit through the air inlet

UNIT "SC"

(spinning cup)



UNIT "CGLC"

(centrifugal gas-liquor
contactor)

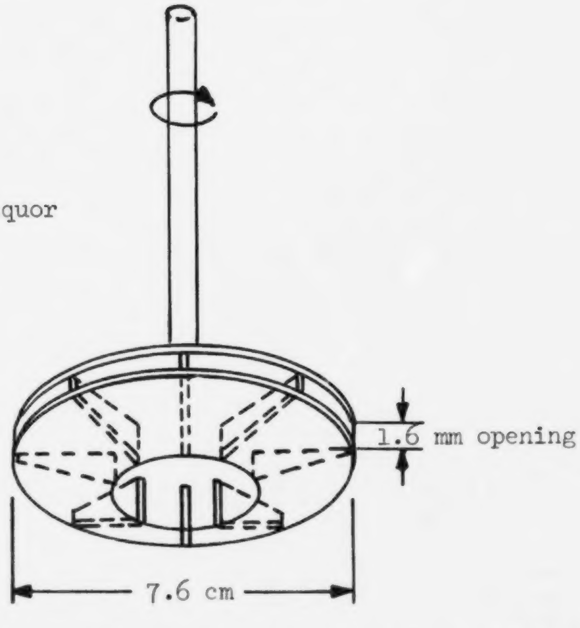

1.6 mm opening
7.6 cm

Figure 5. Oxidizer units used in tests of oxidation of sulfites with air.

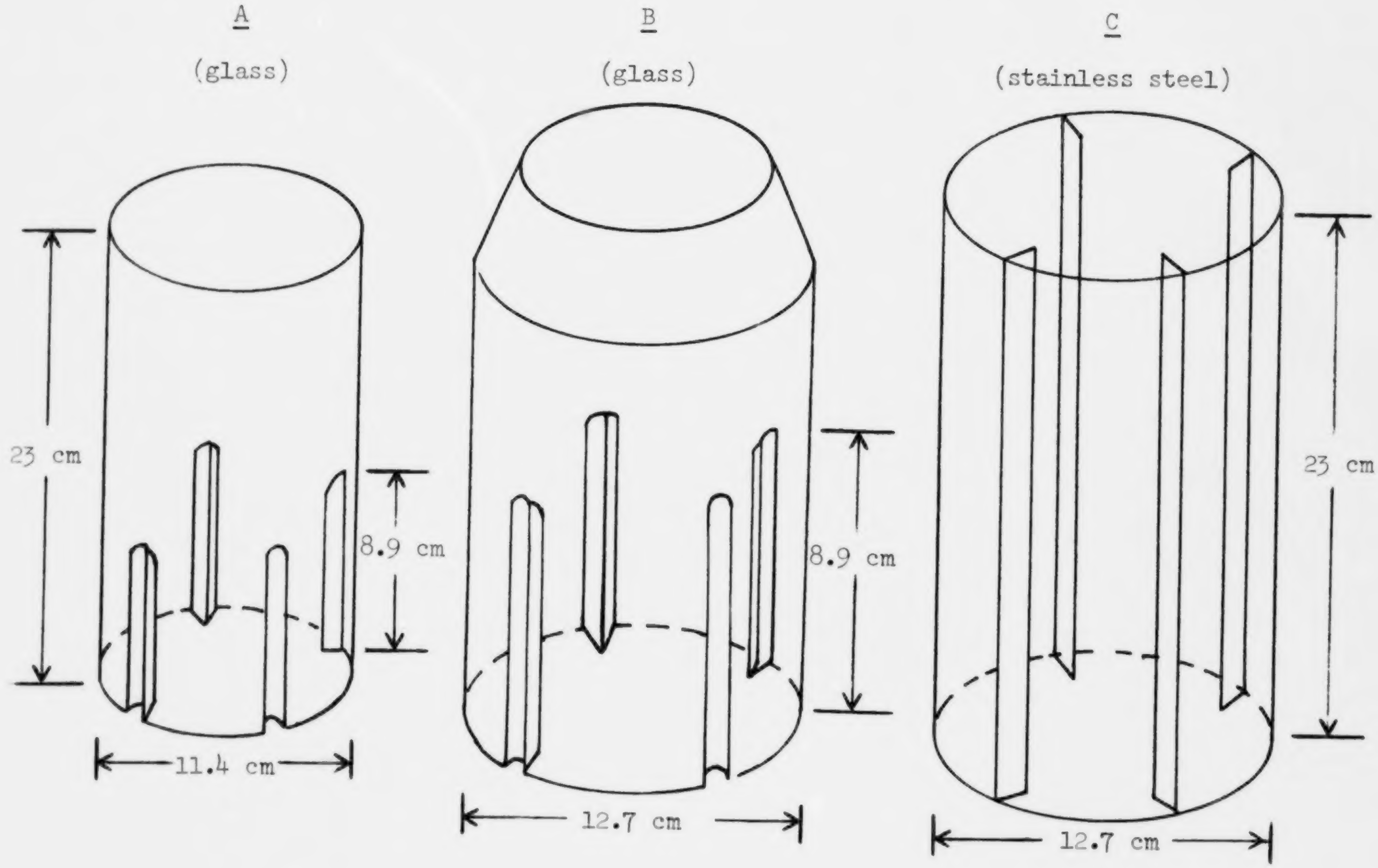

A
(glass)
23 cm
8.9 cm
11.4 cm
B
(glass)
8.9 cm
12.7 cm
C
(stainless steel)
23 cm
12.7 cm

Figure 6. Oxidation vessels used in tests of oxidation of sulfites with air.

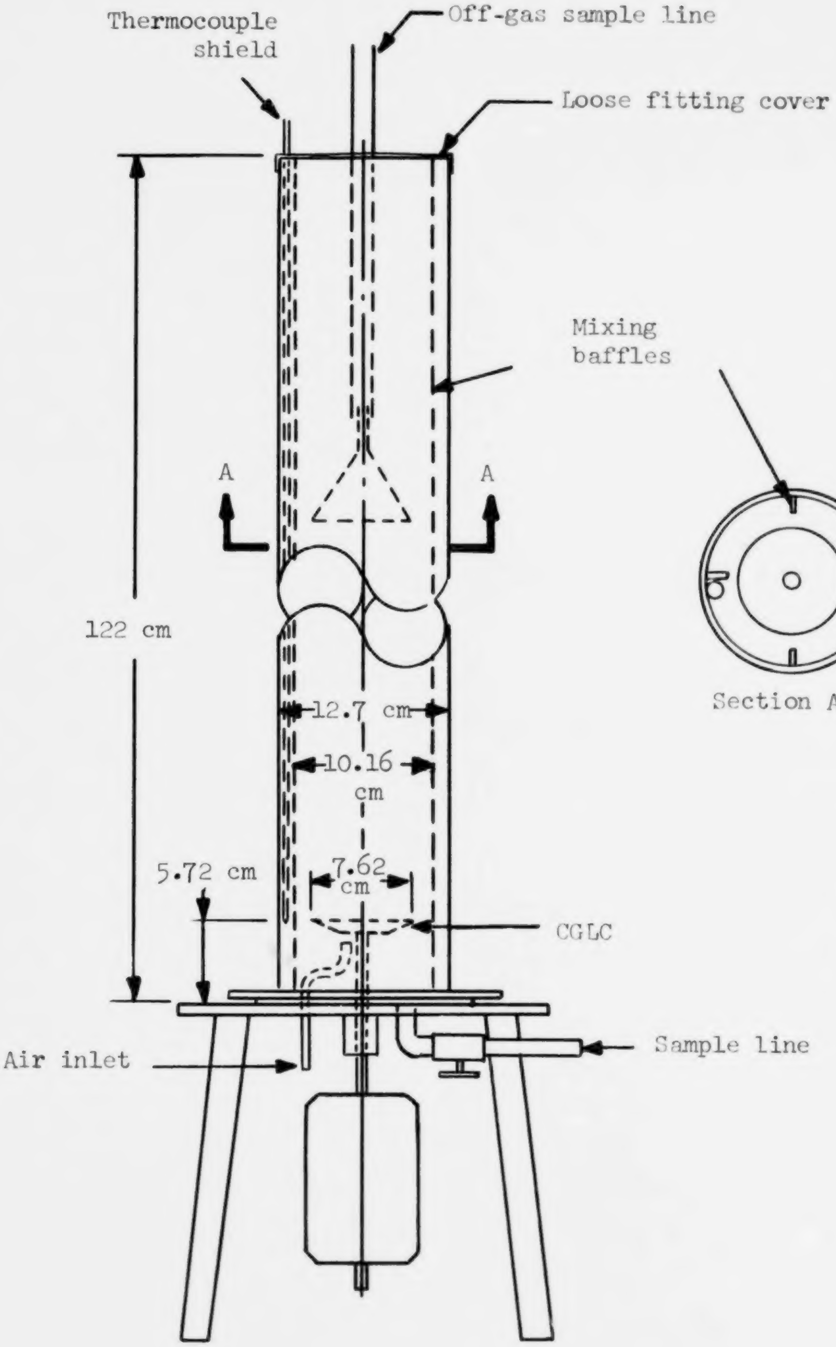

Thermocouple shield
Off-gas sample line
Loose fitting cover
Mixing baffles
A
A
122 cm
12.7 cm
10.16 cm
5.72 cm
7.62 cm
CGLC
Air inlet
Sample line
Section A-A

Figure 7. Tall oxidizer used for study of pool depth.

tube. A continuous measured sample of the off-gas from the oxidizer was pumped through a series of scrubbers and/or dryers to measure the components of the gas or to condition it to allow analysis by gas chromatography of the oxygen content. The torque required to turn the oxidizer units was measured and calculations were made to determine the power requirements for the test. Samples of the fluid being oxidized were withdrawn at timed intervals and analyzed immediately by iodine titration to determine the amount of residual sulfites. The gas chromatograph gave very early indication of the completion of the oxidation process. The pH of the fluid was measured on an intermittent basis.

Calculations then were made of oxidation rates, air utilization, time requirements, power requirements, and power consumption per unit of sulfite oxidized.

SOLUBLE SALT OXIDATION TESTS

The first factor to be studied was the comparison of the two oxidizer units. Comparative tests were planned of the oxidation of ammonium sulfite solutions containing about 60 grams of sulfite sulfur per liter. Ammonium sulfite oxidizes fairly rapidly when stored dry in reagent bottles and is not generally available from chemical supply houses. The ammonium sulfite solutions used in this series of tests, therefore, were made in the laboratory by adding gaseous ammonia to the fairly stable and available ammonium bisulfite solution (45% NH_4HSO_3) to a pH of 7.5 and diluting to the desired concentration. At this pH the solution is essentially ammonium sulfite. Results of these tests are given in Table 6. In the first of these tests (No. 8), the spinning cup (SC) was used to oxidize 1 liter of solution containing 63.2 grams of sulfite sulfur. The air rate, as in all tests, was 4120 milliliters per minute and the cup was turned at 3000 rpm or at a peripheral speed of 8 meters per second (26.2 ft/sec). The torque required to turn the cup at this rate resulted in a 29 mV reading and amounted to 94.92 g-cm. Using the 5.08-centimeter (2-inch) cup, rotated at 3000 rpm, the calculated energy requirement for driving the cup was 29.24 watt-hours per hour of operation. The solution was sampled at intervals and when analysis indicated that oxidation was nearly complete, the test was stopped. More than 12 hours (728 min) was required to accomplish 97.5% oxidation.

Some oxidation apparently occurred during the pretest warmup period in this and the remainder of the tests. In order to eliminate such unintentional oxidation from calculations, oxidation was measured from the first timed sample until the end of the test or until depletion of the sulfite species caused a noticeable change in the oxidation rate. Oxidation appeared to proceed at a nearly constant rate over the periods for which the calculations were made.

In test 8, the period of essentially constant oxidation extended from 108.5 to 728 minutes. During this period, the energy requirement was 181 watt-hours per mole of sulfur oxidized (181 Wh/mole); oxygen utilization amounted to 3.5% of that fed as air into the unit, and the oxidation rate was 0.0027 mole sulfur per minute.

TABLE 6. OXIDATION OF SULFITES--LABORATORY TEST CONDITIONS AND RESULTS

Test No.	8			9			11A			12		
Salt oxidized	$(NH_4)_2SO_3$			$(NH_4)_2SO_3$			$(NH_4)_2SO_3$			$(NH_4)_2SO_3$		
Conc., g SO_2-S/1	63.2			61.7			56.9			55.0		
Volume, 1	1			1			1			1		
Oxidizer												
Rotary unit	SC			CGLC			CGLC			CGLC		
Peripheral speed, m/sec	8			5.6			8			5.6		
Torque, indication, mV	29			49			95			50		
Vessel	G-1			G-2			SS-1			SS-1		
Samples	Time, min	pH	SO_2-S,g/1	Time, min	pH	SO_2-S, g/1	Time, min	pH	SO_2-S, g/1	Time, min	pH	SO_2-S, g/1
1	108.5	7.25	55.5	60	7.35	44.8	30	7.4	35.4	30	7.6	42.8
2	180	7.05	49.8	120	7.15	39.4	60	7.1	26.7	60	7.4	27.8
3	230.6	7.00	41	180	7.00	34.5	90	6.6	14.8	90	7.2	20.9
4	360	6.65	36.9	240	6.70	32.2	120	3.1	4.9	120	6.8	14.8
5	513	6.25	21.6	300	6.42	23.7	150	3.2	1.3	150	5.1	8.3
6	590	5.75	13.8	360	6.70	15.8	180	3.6	1.7	180	3.2	5.9
7	665	3.95	6.6	420	5.45	9.3	210	-	-	210	3.7	5.3
8	728	3.90	2.2	480	3.95	3.2						
9				540	4.10	2.45						
10				600	4.20	1.1						
Constant oxidation period, min	108.5-728			60-480			30-120			30-210		
Energy used, Wh/mole oxidized	181			124			100			60		
Oxygen utilization, %	3.5			4.0			13.8			8.4		
Oxidation rate, mole/min	0.0027			0.0034			0.0106			0.0065		

(continued)

TABLE 6 (continued)

Test No.		13			14			15			16	
Salt oxidized		$(NH_4)_2SO_3$			$(NH_4)_2SO_3$			$(NH_4)_2SO_3$			$(NH_4)_2SO_3$	
Conc., g SO_2-S/l		63.95			40.4			60.9			63.0	
Volume, l		1.5			1.5			1			1	
Oxidizer												
Rotary unit		CGLC			CGLC			SC			CGLC	
Peripheral speed, m/sec		8			8			8			8	
Torque, indication, mV		95			95			29			95	
Vessel		SS-1			SS-1			SS-1			G-3	
Samples	Time, min	pH	SO_2-S, g/l	Time, min	pH	SO_2-S, g/l	Time, min	pH	SO_2-S, g/l	Time, min	pH	SO_2-S, g/l
1	30	7.3	46.0	30	6.85	18.3	60		55.9	30	7.6	56.1
2	60	6.7	30.3	60	6.45	9.8	120		47.2	60	7.5	48.4
3	90	6.65	19.8	90	3.95	6.4	180		46.8	90	7.35	37.1
4	120	5.95	13.4	120	3.6	4.9	210		47.2	120	7.15	30.8
5	150	3.8	8.9	150	3.4	4.5	270		34.0	150	6.95	24.5
6				180	3.8	1.5	360		33.6	210	6.2	9.4
7				210	3.8	1.45	420		29.5	240	3.65	5.7
8				240	3.8	0.96	480		25.4			
9												
10												
Constant oxidation period, min		30-150			30-120			60-480			30-210	
Energy used, Wh/mole oxidized		73			152			210			131	
Oxygen utilization, %		18.8			9.1			3.0			10.5	
Oxidation rate, mole/min		0.0145			0.0070			0.0023			0.0081	

(continued)

TABLE 6 (continued)

Test No.		17			18			19			20	
Salt oxidized		$(NH_4)_2SO_3$			$(NH_4)_2SO_3$			K_2SO_3[a]			K_2SO_3[b]	
Conc., g SO_2-S/1		58.6			56.7			49.8			60.4	
Volume, 1		1			1			1.075			1.0	
Oxidizer												
Rotary unit		CGLC			CGLC			CGLC			CGLC	
Peripheral speed, m/sec		8.8			8			8			8	
Torque, indication, mV		105			95			95			95	
Vessel		G-3			SS-1			SS-1			SS-1	
Samples	**Time, min**	**pH**	**SO_2-S, g/1**	**Time, min**	**pH**	**SO_2-S, g/1**	**Time, min**	**pH**	**SO_2-S, g/1**	**Time, min**	**pH**	**SO_2-S, g/1**
1	30	7.7	53.8	30	7.6	47.0	30	8.5	43.9	30	10.4	58.0
2	60	7.8	45.3	60	-	32.9	60	8.4	33.9	60	10.1	47.5
3	90	7.6	36.6	90	7.0	20.6	90	8.15	19.7	90	9.9	38.9
4	120	7.45	27.6	120	6.2	6.9	120	6.55	1.6	120	9.8	28.3
5				180	3.7	1.7				150	9.6	13.1
6										180	9.55	2.0
7												
8												
9												
10												
Constant oxidation period, min		30-120			30-120			30-120			30-180	
Energy used, Wh/mole oxidized		140			76			67			91	
Oxygen utilization, %		12.0			18.1			20.5			15.1	
Oxidation rate, mole/min		0.0091			0.0139			0.0158			0.0117	

[a] pH 8.5.
[b] pH 10.8.

(continued)

TABLE 6 (continued)

Test No.		24			25			26			38	
Salt oxidized		K_2SO_3			K_2SO_3			K_2SO_3			K_2SO_3	
Conc., g SO_2-S/1		19.6			19.6			21.49			19.0	
Volume, 1		2[c]			4[d]			6[e]			14[f]	
Oxidizer												
Rotary unit		CGLC			CGLC			CGLC			CGLC	
Peripheral speed, m/sec		7			7			7			7	
Torque, indication, mV		100			100			100			100	
Vessel		SS-2			SS-2			SS-2			SS-2	
Samples	Time, min	pH	SO_2-S, g/1	Time, min	pH	SO_2-S, g/1	Time, min	pH	SO_2-S, g/1	Time, min	pH	SO_2-S, g/1
1	10	10.8[g]	18.2	20	10.8[g]	17.3	20	10.8[g]	18.4	60	10.4[g]	15.9
2	20	-	14.8	40	-	13.4	40	-	14.9	120	-	11.44
3	30	-	11.8	60	-	9.1	60	-	11.5	180	-	6.17
4	40	-	9.0	80	-	4.6	80	-	8.4	220	-	2.63
5	50	-	5.5	100	9.95	0.23	100	-	5.3	240	10.3	1.3
6	60	-	3.5				120	-	1.4			
7	70	-	0.3				140	9.8	0.4			
8	80	9.65	0.05									
9												
10												
Constant oxidation period, min		10-70			20-100			20-120			60-220	
Energy used, Wh/mole oxidized		53			37			31			27	
Oxygen utilization, %		24.1			34.5			41.3			47.0	
Oxidation rate, mole/min		0.0186			0.0267			0.0319			0.0362	

[c] Pool depth 15.25 cm (6 in).
[d] Pool depth 31.75 cm (12.5 in).
[e] Pool depth 48.25 cm (19 in).
[f] Pool depth 111.25 cm (43.8 in).
[g] pH of solution prior to start of test.

During test 8, off-gases from the oxidizer were passed through scrubbers to determine the amounts of ammonia and sulfur dioxide being lost and the portions of the test over which the losses occurred. Ammonia loss was detected as soon as the feed of air was begun and continued at a decreasing rate until a pH of about 6 was reached (about 9 hr). The total ammonia loss amounted to about 0.02 mole or 0.5% of the input amount. Sulfur dioxide loss began at a detectable rate after the pH reached 6.65 (6 hr) and continued at an increasing rate until the test ended (pH 3.9, 12 hr). The total loss of SO_2 detected amounted to 3.9% of that present at the beginning of the test. The losses were fairly low (0.04 g NH_3 and 0.83 g SO_2/hr) and were not measured in later tests where time was much shorter. There was, however, no time during the test when one of the species was not being volatilized and between the pH's of 6.65 and 6; some of both were detected in the off-gases.

A test was attempted in the same vessel using the centrifugal gas-liquor contactor (CGLC) but the clearance between the rotary unit and the baffles was so small that the unit bumped the baffles when rotated, even at 5.6 meters per second (1400 rpm), and the test was stopped. A larger glass vessel (G-2) was built in which the clearance was the same as in the smaller unit when the spinning cup was in use. Test 9 was made in the larger glass unit using the CGLC with a rotational speed of 1400 rpm or 5.6 meters per second peripheral speed and an original sulfite concentration about the same as in test 8. Oxidation was essentially constant over the period 60 to 480 minutes after which about 95% of the sulfur had been oxidized. The energy requirement over the period was 124 watt-hours per mole oxidized, oxygen utilization was 4% of that fed, and the oxidation rate was 0.0034 mole per minute. There was an improvement in air and energy utilization using the CGLC although the peripheral speed was not the same.

A stainless steel tank with sharp-edged, full height baffles was fabricated (SS-1) in which the CGLC could be operated at high speeds. Test 11A was made in this vessel using the CGLC at a peripheral speed of 8 meters per second (2000 rpm) and 1 liter of ammonium sulfite solution containing 56.9 grams sulfite sulfur per liter. Oxidation occurred much more rapidly than in tests 8 and 9. Even though a large part of the sulfite was oxidized in the warmup period, oxidation during the period of constant oxidation occurred at the rate of 0.0106 mole per minute, an increase of about 300% over test 9. Energy consumption was reduced to 100 watt-hours per mole and oxygen utilization increased to 13.8%.

Test 15 was made to check the results of test 8 to determine if the very slow oxidation with the spinning cup was reproducible. Oxidation rates, oxygen utilization values, and energy requirements were comparable.

In order to determine whether the improvements in test 11A were due to the peripheral speed of the CGLC or to the material of construction and/or configuration of the tank, test 12 was made at a peripheral speed of 5.6 meters per second as in test 9. The result was a two-fold increase in oxidation rate and oxygen utilization coupled with a 50% decrease in energy utilization (test 12 vs. test 9). A large part of the increased effectiveness was due to the configuration or material of construction of the tank.

A tank was constructed of glass and plastic (G-3) to simulate the configuration of the stainless steel tank. Test 16 was made in this tank using conditions otherwise the same as in test 11A. Energy requirement was greater and both oxidation rate and oxygen utilization values were lower when the nonmetallic vessel was used. The use of the metallic vessel apparently catalyzed oxidation.

Test 17 was made using the same equipment as test 16 (CGLC in nonmetallic tank) but with the highest peripheral speed allowable (88 m/sec) with the drive system employed. Oxidation rate and oxygen utilization were increased but the energy rate per mole of sulfur oxidized was increased slightly.

Tests 13 and 14 were made in the stainless steel tank using the CGLC at 8 meters per second; the pool volume and concentration were varied. Increasing volume (1.5 l, test 13 vs. 1.0 l, test 11A) decreased energy requirement and increased oxidation rate and oxygen utilization values. Apparently the increased pool depth and consequent greater retention time of the air in the pool made these differences. Decreasing concentration (40.4 vs. 63.95 g sulfite sulfur/l, test 14 vs. test 13) increased the energy requirement and decreased both oxidation rate and oxygen utilization values. Apparently the total salt concentration rather than the sulfite concentration made the difference since, in all cases, the rate of oxidation remained essentially constant until the sulfite sulfur concentration had decreased to values well below the initial value of this test.

Test 18 was made to duplicate test 11A. Results were fairly consistent, the primary differences being caused by the indicated proportion of sulfite oxidized before the first sampling time. After 180 minutes in both cases, the residual sulfite sulfur analysis was 1.7 grams per liter and the pH was about 3.7. Indicated oxidation over the period 30 to 120 minutes varied from about 30 grams to about 40 grams because of the variation of analysis in the first samples. This caused the variations in power requirements (100 vs. 76 Wh/mole) and in oxidation rate (0.011 vs. 0.014 mole/min).

Two tests were made in which 2 molar potassium sulfite solutions were oxidized. Reagent potassium sulfite is available and was used in these tests. The potassium sulfite solution used in test 19 had a pH of 8.5 and contained considerably less than the calculated sulfite sulfur content; that used in test 20 had a pH of 10.8 and was closer to the calculated composition. It was probable that the material used for test 19 had oxidized in storage; such would account for the lower pH and reduced sulfite sulfur content. However, since the pH of potassium sulfite was not known, it was decided to determine the value for both the sulfite and the bisulfite. Similar determinations were made for ammonium sulfite and bisulfite. To determine the desired pH values, tests were made in which 0.2 N potassium and ammonium hydroxide solutions were reacted continuously with pure sulfur dioxide gas in a closed vessel and the pH values were recorded continuously. The pH values were measured using a Broadley-James sealed combination pH electrode, calibrated with Beckman pH 7 buffer solution, and read with a Beckman Model 1055 recording pH meter. The results of these two titrations are shown in Figure 8 and are tabulated below.

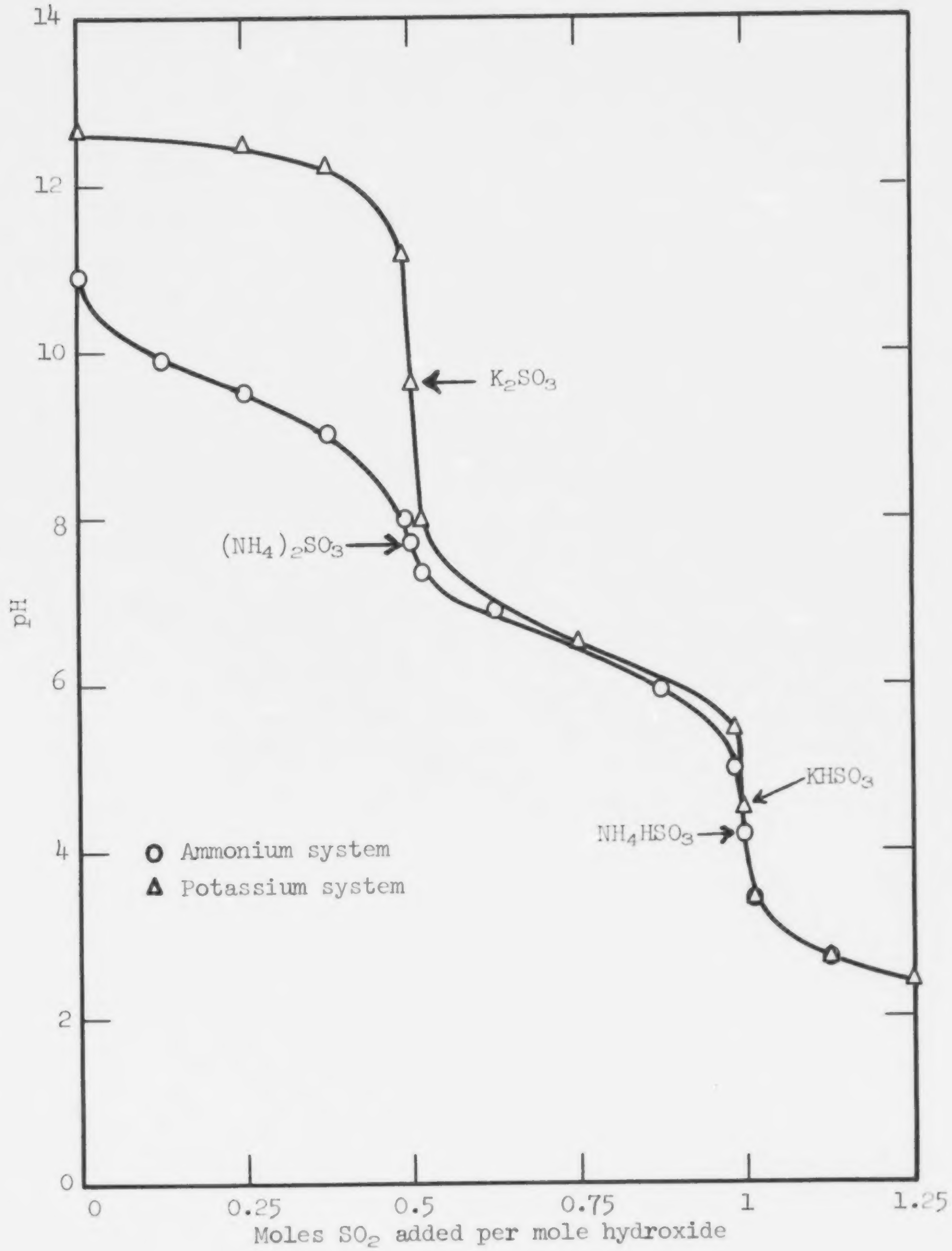


Figure 8. pH during reaction of 0.2 N ammonium and potassium hydroxides with sulfur dioxide.

	pH	
	Range	Center point
Salt		
K_2SO_3	8.0-11.2	9.6
$KHSO_3$	3.5-5.5	4.5
$(NH_4)_2SO_3$	7.4-8.0	7.7
NH_4HSO_3	3.4-5.0	4.2

In test 19, with the initial pH at 8.5, oxidation proceeded at the rate of 0.0158 mole per minute, oxygen utilization was 20.5%, and the energy requirement was 67 watt-hours per mole. In test 20, with the initial pH at 10.8, oxidation was less rapid, 0.0117 mole per minute, oxygen utilization was 15.1%, and the energy requirement was 91 watt-hours per mole. Apparently oxidation proceeded more rapidly at the lower initial pH although no reason for this is obvious.

A comparison of the results of test 20 using the better potassium sulfite with test 18 in which ammonium sulfite was used indicates that the oxidation rate of the potassium sulfite might be slightly lower than for the ammonium sulfite; however, the indicated difference was small.

In the preceding tests, the volume of material being oxidized was limited to about 1.5 liters by the size of the oxidation vessel and the static depth of the pool was limited to about 23 centimeters (9 in). In most tests, the pool depth was 8.25 centimeters (3-1/4 in) and the CGLC was mounted so that its discharge was at the midpoint of the pool or about 4.76 centimeters (1-7/8 in) from the bottom of the tank. The CGLC was mounted on a shaft that entered the tank from the top; a "J" shaped air tube also entered from the top of the tank and directed air to an inlet in the bottom of the CGLC where mixing with fluid was initiated.

A study of the effects of greater pool depth required a new oxidizer tank and the mounting of the CGLC on a shaft extending through the bottom of the tank in order to shorten the shaft and to eliminate the need for a line bearing on the shaft; see Figure 7. This arrangement required a seal on the shaft and therefore introduced some friction that did not exist in the shorter version of the oxidizer tank. The new tank was built to the same diameter (12.7 cm or 5 in) and cross section configuration as the smaller tank but was 122 centimeters (48 in) deep and the four mixing baffles (1.3 cm or 1/2 in wide) extended to the full depth. The off-gas from the pool was allowed to escape through a partially closed cover to minimize backmixing with outside air; off-gas samples were withdrawn through an inverted funnel suspended just above the pool surface to minimize mixing with the air in the chamber above the sampling point. The air fed to the unit was metered by a rotameter and introduced through a tube extending through the bottom of the tank to a point below the inlet of the CGLC which was mounted so that its discharge was 5.72 centimeters (2-1/4 in) from the tank bottom. The temperature of the solution was measured by a thermocouple placed near the wall of the tank and at the level of the CGLC outlet and was controlled at about 52°C (125°F) by addition of heat from a heating tape wrapped on the tank or by the removal of heat with a stream of compressed air directed on the outside surface of the tank.

A series of four tests was made in which approximately 0.6 molar potassium sulfite solution (about 19 g sulfite sulfur/l) was treated with 4120 cubic centimeters of air per minute through the CGLC unit operated at 1750 rpm. Operation at 2000 rpm could not be maintained because of the increased power required to overcome the friction of the shaft seal and the limited power of the drive system. Samples were taken by withdrawing solution through a valve at the bottom of the tank, pipetting a known volume from the sample for analysis, and returning the remainder to the oxidizer; the tests were not stopped for sampling. Sampling frequency was varied with the solution volume; samples were taken at 10-minute intervals when the tank contained 2 liters of solution, 20-minute intervals for 4 or 6 liters, and 60-minute intervals for 14 liters. The air rate was sufficient to supply the oxygen equivalent of 0.07725 mole of sulfur dioxide per minute or about 12.5% of the oxygen equivalent of 1 liter of the solution. Thus, in the 2-liter test, the approximate stoichiometric amount of oxygen was supplied each 16 minutes, 4 liters required 32 minutes, 6 liters required 48 minutes, and 14 liters required 122 minutes. The times are approximate because of variations in input solution analysis.

Data from the tests are given in Table 6 and Figures 9-13. Figures 9 and 10 show, versus time, sulfite sulfur oxidation as percent of input sulfite sulfur and as moles, respectively. The response was essentially linear in both cases (Figures 9 and 10) and shows a continuous increase in the amount oxidized until oxidation reached about 95% or more (Figure 9). The average rate of oxidation (moles/min) increased with pool depth (Figure 11). Since the oxidation rates did not decrease perceptably until a high degree of oxidation (probably $> 95\%$) had been accomplished, production of sulfates essentially free of sulfites should be attainable.

Figure 12 shows the energy requirements per mole of sulfite oxidized as measured with a torque meter versus pool depth. The energy required to overcome the friction of the seal has been eliminated from these values. Since approximately the same torque was required to turn the CGLC regardless of the pool depth, the energy requirements decreased as the pool depth and oxidation rates increased.

Figure 13 shows average oxygen utilization over the period of steady oxidation rates versus pool depth. The curve is similar to that for oxidation rate, moles per minute, since the air rate was the same in all tests. Best utilization occurred at the greatest depth as might be expected but improvement leveled off at volumes greater than 6 liters (48 cm or 19 in depth). Perhaps the most optimistic note is the very high oxygen utilization attained in these tests with the CGLC unit. Almost 42% oxygen utilization was attained in about 48 centimeters of pool depth. It is reported that as much as 14 meters or 45 feet of pool depth is used to attain similar utilization with the spinning cup. However, the effects of solution concentration, cation identity, oxidation promoters or retarders, and tank geometry are not well known with either oxidizer and may affect the comparison. Continuous tests have not been made with the CGLC.

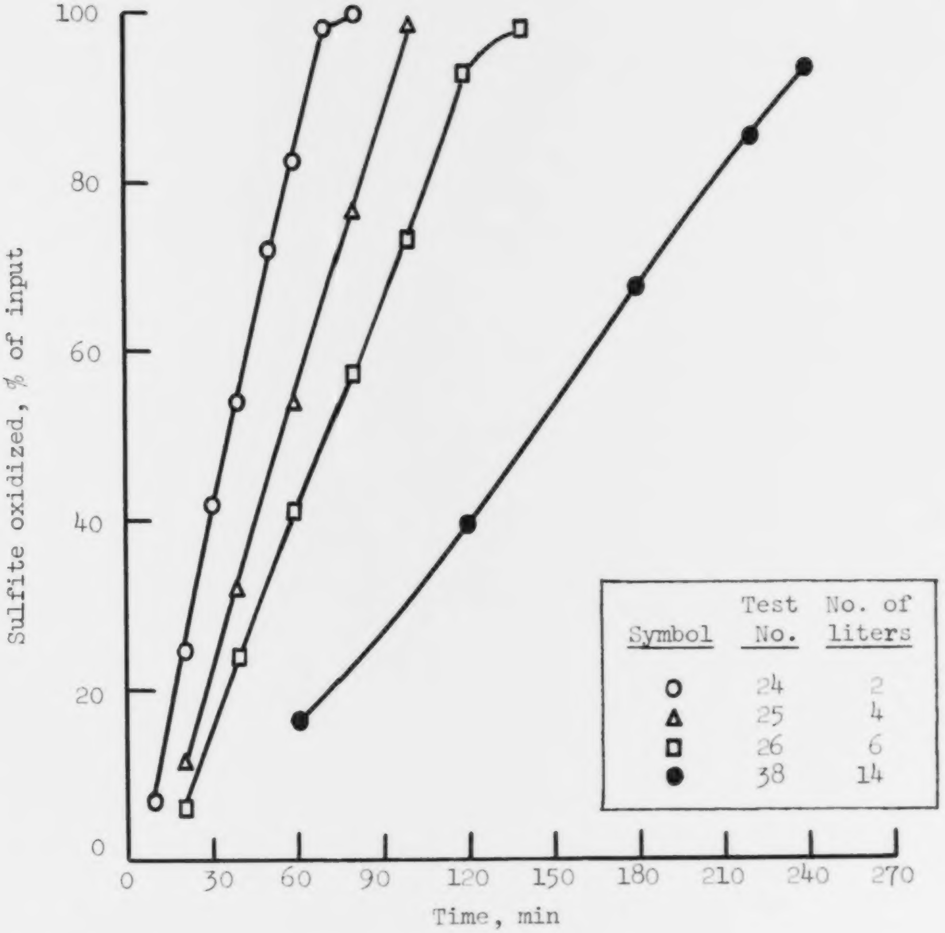


Figure 9. Effect of time on proportion of sulfite oxidized.

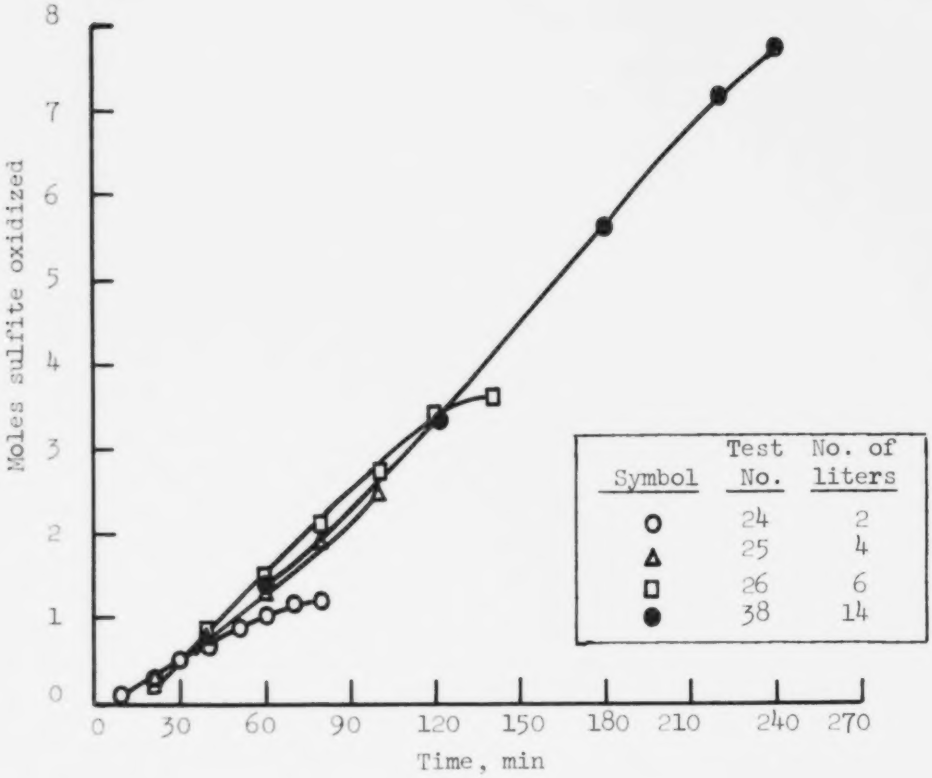


Figure 10. Effect of time on moles of sulfite oxidized.

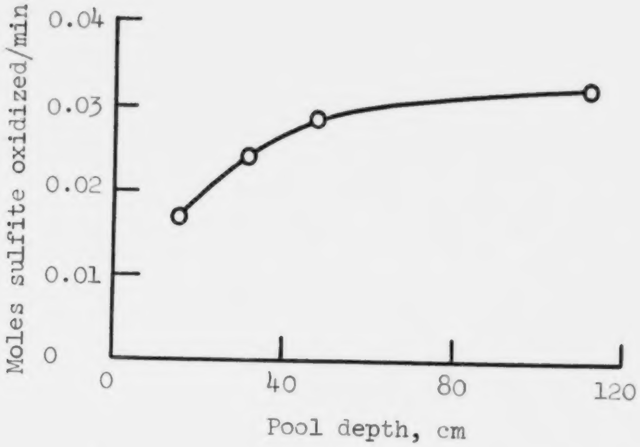


Figure 11. Effect of pool depth on rate of oxidation.

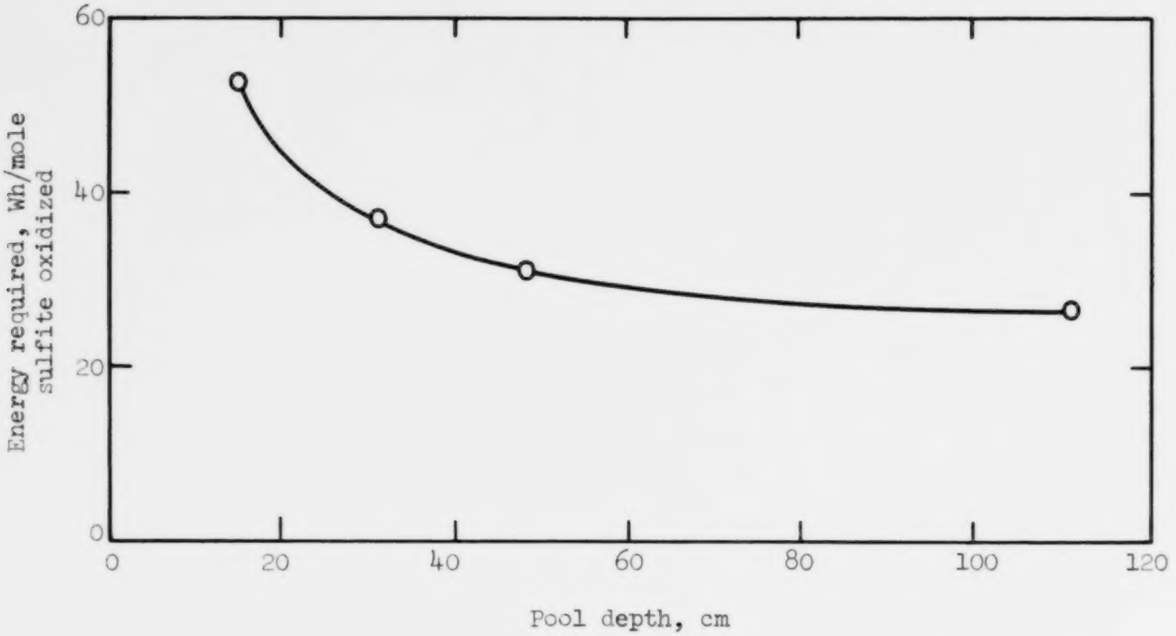


Figure 12. Effect of pool depth on energy required per mole of sulfite oxidized.

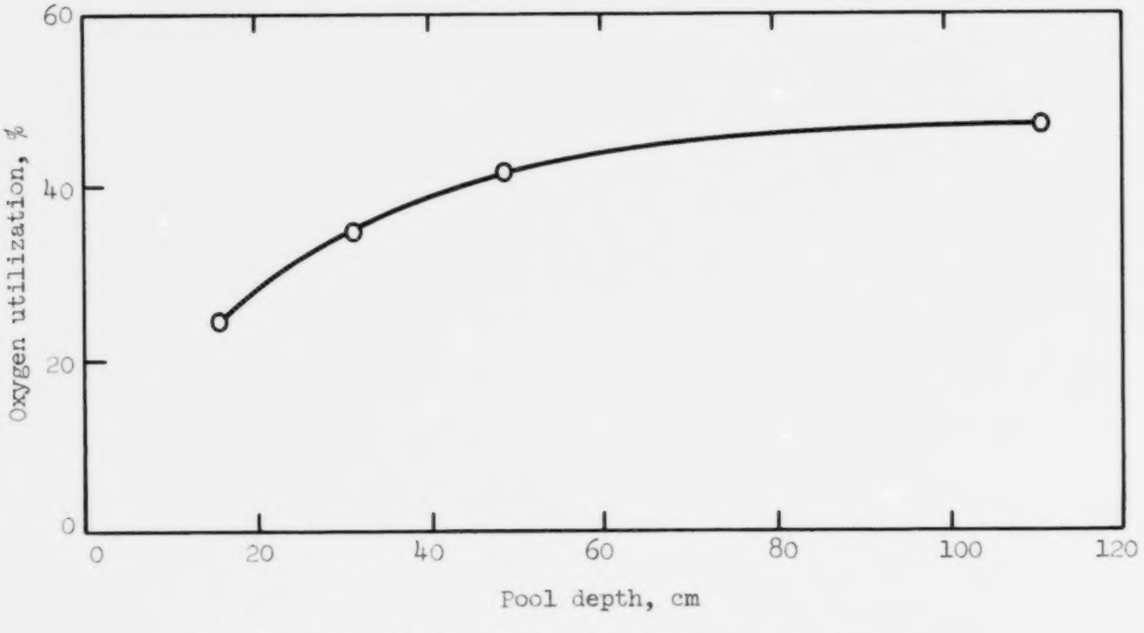


Figure 13. Effect of pool depth on oxygen utilization.

Results of these tests indicate that the CGLC is a very effective oxidizing device and that, at the conditions employed, a shallow tank can be used effectively. Therefore, the use of such a device should offer means of reducing energy requirements and costs for pumping and storing liquids, for compressing air, and for turning the oxidizer unit. Also, shaft seals would not be required to withstand as much pressure or might be eliminated in large units by using top-entry shafts.

OXIDATION OF OTHER SALTS

Oxidation of slurries of other salts having lower solubilities than ammonium or potassium sulfites were made using the CGLC in the short stainless steel tank.

Zinc Sulfite

Oxidation of zinc sulfite is of interest because of the relatively low temperature at which zinc sulfate decomposes to give zinc oxide (for recycle to a scrubber) and sulfur trioxide (which may be absorbed in water to form sulfuric acid). A process has been described (Slack, A. V., to Petrusek, R. A. "Removal of Sulfur Dioxide from Stack Gas by Scrubbing with Zinc Oxide Slurry," memorandum, January 27, 1971) in which this series of stages is included; it would allow the production of sulfuric acid from stack gas sulfur dioxide and eliminate the vanadium-catalyzed oxidation step required in the usual sulfuric acid process.

The oxidation of zinc sulfite is unusual in that the sulfite is a fairly insoluble material (0.16 g $ZnSO_3 \cdot 2H_2O$/100 g H_2O) while zinc sulfate is highly soluble (57.45 g $ZnSO_4$/100 g H_2O at 25°C). This, of course, means that oxidation tests will start with a slurry of zinc sulfite and will end with a solution of zinc sulfate; any zinc sulfate available for thermal decomposition would have to be obtained by crystallization from the final solution.

Obtaining zinc sulfite was a problem. The material is not generally available in the chemical supply catalogs. A supply, therefore, was prepared in the laboratory by reacting a zinc acetate solution with sulfur dioxide gas and recovering the zinc sulfite by vacuum evaporation of water and acetic acid. In preparation of this material, 1 pound of zinc acetate dihydrate was dissolved in 9 liters of water and pure gaseous sulfur dioxide was bubbled into the solution until the pH decreased to 4.15. The reaction frees acetic acid and forms zinc sulfite dihydrate as follows:

$$Zn(CH_3COO)_2 \cdot 2H_2O + SO_2 \longrightarrow 2CH_3COOH + ZnSO_3 \cdot 2H_2O$$

The zinc sulfite is soluble in the weak acetic acid produced. Water and acetic acid therefore were boiled off under vacuum to recover the zinc sulfite in the dihydrate form in which it is stable at room temperature. A vacuum of about 63 to 68 centimeters (25-27 in) mercury was maintained during the evaporation step. As zinc sulfite dihydrate ($ZnSO_3 \cdot 2H_2O$) precipitated, the slurry in the evaporator was filtered (without allowing the solution to contact room air) and the solid product was washed with alcohol and dried with air. Samples were analyzed by infrared analysis and by the petrographic microscope. About 111 grams of $ZnSO_3 \cdot 2H_2O$ was collected before any significant amount of foreign material appeared in the precipitate. Chemical analysis of the $ZnSO_3 \cdot 2H_2O$ showed it to contain 16.7% total sulfur, 16.7% sulfite sulfur, and 34.2% zinc. The analyses are 94.7% of theoretical and the zinc to sulfur mole ratio is 1.002. Apparently there was a small amount of moisture or alcohol left in the sample. The average length of the particles was about 10 microns; this length generally ranged from about 1 micron to 50 microns, the width was generally about 60% of the length, and the thickness about 20% of the length.

Oxidation tests were made with 1 and 5% slurries of the $ZnSO_3 \cdot 2H_2O$ in water at 52°C. One liter of slurry was used in each test; the pH was not adjusted. Air was introduced into the CGLC at 4120 milliliters per minute. Samples were withdrawn each 10 minutes and analyzed iodometrically for sulfite sulfur. Evaluation was made on the basis of these analyses.

In the first test, the slurry was sampled as soon as the 1% slurry was formed and the analysis (1.618 g sulfite sulfur/l) was close to that expected (1.67 g/l); it was indicated, however, that as much as 3% of the sulfur had been oxidized in the short time required to suspend the solids. Suspension was attained by rotating the CGLC without air feed for a short time, probably less than half a minute. The pH of the slurry at the beginning of the test was 6.1. Oxidation proceeded as indicated in the following tabulation, which also includes data for test 2, described later.

Time, min	pH	Sulfite sulfur content, g/l	Sulfite sulfur oxidized % of input	 Mole/min	Oxygen utilization, %
Test 1					
Input	-	1.67	-	-	-
0	6.1	1.62	3	-	-
10	4.8	0.26	84	0.00425	5.5
20	5.0	0.17	90	0.00028	0.4
30	5.0	0.08	95	0.00028	0.4
Test 2					
Input	-	8.35	-	-	-
0	5.4	3.29	61	-	-
10	5.1	0.58	93	0.00846	11.0
20	5.1	0.27	97	0.00096	1.2
30	4.9	0.14	98	0.00040	0.5

The air feed per minute was sufficient to oxidize 0.0773 mole of sulfite sulfur, which would be equivalent to 153% of the sulfite sulfur present. Thus, in 10 minutes, the time of the first sample, 15.3 times stoichiometric air had been fed and 84% of the sulfur dioxide had been oxidized; oxygen utilization thus was about 5.5%.

In test 2, preparation of the more concentrated (5% vs. 1%) $ZnSO_3 \cdot 2H_2O$ suspension required more time, and oxidation apparently proceeded to about 61% completion during this time; however, errors in sampling the slurry could have been involved. After 10 minutes of operation, the material was 93% oxidized. Since the air feed per minute now was equivalent to only about 30.6% of that required to oxidize all the sulfite sulfur present, the oxygen utilization (0-10 min, 61-93% oxidation) was about 11%. The affinity for oxygen is indicated by the very rapid oxidation rate, even in the suspending step. Initial oxidation in test 2 was indicated also by the low pH of 5.4 at the beginning of the test.

It is concluded that the oxidation of zinc sulfite was accomplished fairly rapidly and easily with the CGLC and that its solubility is great enough that no adjustment of pH would be required to maintain a suitable rate. Recovery of the sulfate salt in solid form for disposal or use will require removal of significant amounts of water; the solubility of zinc sulfate is fairly high and it may precipitate with as many as 7 moles of water of hydration. No data were developed related to the maximum zinc sulfite slurry concentration allowable in the oxidizer.

Calcium Sulfite

Oxidation of calcium sulfite ($CaSO_3$) produced in lime or limestone-sulfur dioxide scrubbers is desirable for several reasons. Major benefits of oxidation would be (1) the formation of a material suitable for landfill that will dewater more readily and completely than will $CaSO_3$ and (2) the obviation of any continued chemical oxygen demand in the discarded waste material. In prior work (August 1972 Applied Research Branch report, TVA), the oxidation of $CaSO_3$ was shown to respond to initial pH and to the presence of several iron salts as catalysts. In those tests, made with the spinning cup oxidizer and in Pyrex, the oxidation rate of 1% $CaSO_3$ slurries was low when the pH was at 5 or above; about 1 hour and 20 times stoichiometric air were required to accomplish 87% oxidation at pH 5. A series of laboratory-scale tests now has been made in which $CaSO_3$ slurries were oxidized with the CGLC oxidizer in a stainless steel tank.

Calcium sulfite for the tests was produced in the laboratory by reacting a solution of calcium acetate with sulfur dioxide gas. Aqueous acetic acid was a byproduct. Precipitated $CaSO_3$ was filtered from the aqueous acetic acid, washed with water, and dried. Chemical and petrographic analyses were made. The material contained 42.8% calcium oxide and 24.3% sulfur (theoretical values for $CaSO_3 \cdot 1/2H_2O$ are 43.4 and 24.8%, respectively); about 4% of the sulfur was oxidized to sulfate form. Petrographically, the material was described as agglomerates of small (less than 1 micron) crystals of $CaSO_3 \cdot 1/2H_2O$ having a mean index of refraction of 1.604. The crystals are oriented within the aggregates indicating that they have an elongated direction along which they have collected during assemblage. The aggregates range up to 200 microns in diameter.

Oxidation tests were made with 1 and 5% slurries of the laboratory-prepared $CaSO_3 \cdot 1/2H_2O$ using the CGLC at 2000 rpm in the 12.7-centimeter-diameter by 23-centimeter-tall (5-in-dia by 9-in-tall) stainless steel tank. The air rate was 4120 milliliters per minute and the slurry temperature was 52°C in all tests. Slurry samples were analyzed iodometrically to determine residual sulfite content and to allow calculation of the extent of oxidation.

The energy requirement was calculated from measurement of the torque required to turn the oxidizer. Variables in the tests, in addition to the slurry concentration, were initial pH (adjusted by sulfuric acid addition) and addition of ferrous carbonate ($FeCO_3$) as a catalyst. Sulfuric acid was used for pH adjustment to eliminate the effect of other ions in the test and to maintain sulfur dioxide at a known input level. Data from the tests are given in Table 7.

The first three tests (not in table) were made with 1% slurries. Oxidation was much more rapid than in the tests reported in the August 1972 Applied Research Branch report (TVA), reaching 67% in 30 minutes and 96% in 1 hour when the initial pH was 6. When the pH was reduced to 5, oxidation was nearly complete (99%) when the first sample was taken at 30 minutes; the addition of 0.1% $FeCO_3$ at a pH of 5 resulted in 95% oxidation within 10 minutes. These tests were too short and were not sampled frequently enough to determine the relative oxidation rates.

Tests then were made with 5% slurries in order to lengthen the tests enough to obtain meaningful oxidation rates for comparison. In the first of these tests (test 27; Table 7), the pH was adjusted to 6 prior to start of oxidation, and the test was continued for 4 hours. There was some difficulty in sampling due to settling during sample collection as is indicated by a wide scattering of data. In the 1% slurry tests, sampling by pipette had been suitable, but in these tests with 5% slurry, the solids tended to stop up the pipette tip and samples tended to be low in solids. Values obtained early in the test were in error due to this problem and, since most of the sulfite was in solid form, analysis for sulfite sulfur indicated high oxidation values. Analyses were made during the test, however, and the discrepancy was noted; in samples taken after about 30 minutes, special care was taken in the sampling procedure to try to prevent the problem. Subsequent tests were made with a dipper-type volumetric sampler to further reduce the inaccuracy in slurry sampling. Data for the latter part of test 27 appear to be fairly accurate. Although not considered completely accurate, the probable final degree of oxidation was less than about 10%, and the energy requirement was over 5000 watt-hours per mole (Wh/mole) of sulfur dioxide oxidized. The oxidation rate was only about 0.0001 mole per minute. Calculated oxygen utilization was less than 0.2%.

Test 28A was made with the pH adjusted to 5.0 prior to the test and using the revised sampling method. Essentially complete oxidation was achieved in 50 minutes; almost 40% of the sulfite sulfur had either been lost or oxidized prior to start of the air feed. The procedure here was to add the $CaSO_3$ to the water and adjust the pH prior to heating the slurry to test temperature. Slow circulation of the slurry during heating was accomplished by running the CGLC at about 200 rpm. Contact with air at the surface caused some oxidation, and loss of some sulfur dioxide probably occurred prior to the beginning of air feed and high speed rotation of the CGLC; the combination of these factors amounted to 40% of the input sulfite. Test results were evaluated on the basis of incremental oxidation only, however, and are considered valid. The oxidation rate for the test period before 90% oxidation was reached was 0.006 mole of sulfite per minute. During that period, the energy requirement was 176 watt-hours per mole of sulfite oxidized, and oxygen utilization, based on slurry analysis, averaged 7.9%.

TABLE 7. OXIDATION OF CALCIUM SULFITE[a] BY AIR (LABORATORY TESTS)

Test No.	Time, min	pH	SO_2 oxidized, %	Cumulative values			
				Time period, min	Energy required, Wh/mole oxidized	Oxidation rate, mole/min	Oxygen utilized, %
27	0	6.0	-[b]				
	30	6.1	-[b]				
	60	6.05	3				
	90	6.05	1				
	120	6.1	3				
	240	6.4	6	90-240	8240	0.0001	0.16
28A	0	5.0	40				
	10	5.1	59				
	20	5.2	74				
	30	5.1	90	0-30	176	0.0061	7.9
	40	4.8	98				
	50	4.7	99				
30A[c]	0	5.0	14				
	10	4.9	24				
	20	4.9	42				
	30	4.9	56				
	40	4.9	72				
	50	4.9	82	0-50	217	0.0050	6.5
	60	4.9	93				
29A	0	4.00	18				
	10	4.10	82	0-10	46	0.0234	30.3
	20	2.75	98	0-20	73	0.0147	19.0
	30	2.70	99				

[a] 5% slurry of laboratory-prepared $CaSO_3 \cdot 1/2H_2O$.
[b] Values erroneous, see text.
[c] Ferrous carbonate added (0.1% by wt.).

In test 30A, 0.1% $FeCO_3$ was added to the 5% $CaSO_3 \cdot 1/2H_2O$ slurry, and the pH again was adjusted to 5 with sulfuric acid. The analysis of the initial solution indicated that about 14% of the sulfite had been oxidized or lost prior to the beginning of the test. A shorter time was used to heat the slurry than in the preceding test. Oxidation proceeded at about 0.005 mole of sulfite per minute until the test was stopped at 60 minutes. Measurements taken during the first 50 minutes of the test showed that oxidation had reached about 82%, the energy requirement was 217 watt-hours per mole of sulfite oxidized, and average oxygen utilization was 6.5%.

Test 29A was made to duplicate test 28A except that the initial pH was adjusted to 4. About 18% of the sulfite was shown to be oxidized or lost prior to the test; thereafter, the proportion oxidized increased to 82% at 10 minutes and 98% at 20 minutes. During the first 10 minutes, the oxidation rate was 0.023 mole per minute, the energy requirement was 46 watt-hours per mole of sulfite oxidized, and average oxygen utilization (calculated from slurry analysis) was about 30%. On extending the test period to 20 minutes, the oxidation rate (during the 20-min period) was 0.015 mole per minute, the energy requirement was 73 watt-hours per mole of sulfite oxidized, and oxygen utilization was about 19%.

The results of these tests indicate that the CGLC device is suitable for oxidizing $CaSO_3 \cdot 1/2H_2O$, that the oxidation rate is very slow at pH 6 but becomes more rapid as the pH is decreased to 5 or below, that oxidation proceeds about four times as rapidly at pH 4 as at pH 5, and that the addition of $FeCO_3$ at pH 5 does not increase the oxidation rate when the process is carried out in a stainless steel vessel (presumably the stainless steel surface provides the catalyst that was evidenced by the $FeCO_3$ in a glass vessel in the earlier tests).

It appears evident that oxidation of actual solids from lime or limestone scrubbing of sulfur dioxide will require some accommodation of any residual calcium carbonate in order to oxidize the calcium sulfite to calcium sulfate, otherwise the pH would be too high for a reasonable rate. It is possible, however, to gain the required acidity from the stack gas through staged scrubbing; such was reported by R. H. Borgwardt, U.S. Environmental Protection Agency, at the Flue Gas Desulfurization Symposium at New Orleans in March 1976. Tests using actual scrubber solids should be made to study the effects of impurities and the larger $CaSO_3 \cdot 1/2H_2O$ particle size in the actual slurry.

SELECTIVE PRECIPITATION OF SULFATE WITH BARIUM SALTS

Regenerative soluble salt scrubbing processes for removal of sulfur oxides from waste gases usually are affected adversely by sulfates in the system. In most double-alkali systems, the regenerant reacts with the soluble bisulfite from the scrubber in preference to the sulfate, which then builds in the system. Sulfite will react with sulfur dioxide in the scrubber, but sulfate will not. The same type of problem exists in systems where the bisulfite scrubber product is stripped of sulfur dioxide by thermal means. Sulfate, whether formed by disproportionation in the thermal processes or by normal oxidation, builds in the system and eventually will reach saturation; the sulfate then will precipitate and may cause fouling at some point in the system. Some method of removing sulfate is required to prevent its buildup.

During some of the previous small-scale scrubbing tests, attempts were made to monitor the total sulfur content of the solutions by precipitation with barium salts and to determine the degree of oxidation by infrared analysis of the precipitates. In this work, it was noted that barium salts exhibited some selectivity in precipitation and that sulfates were precipitated more readily than sulfites. From these observations, a process was visualized for removal of sulfates from scrubber solutions by the addition of barium carbonate to take advantage of that selectivity. The precipitated barium sulfate, along with any coprecipitated barium sulfite, would be reduced to barium sulfide and subsequently reacted with water and carbon dioxide to form barium carbonate and hydrogen sulfide. Reduction of barium sulfate and conversion to barium carbonate is a commercially practiced process. The barium carbonate would be recycled; the hydrogen sulfide would be used to produce sulfur by the Claus process. Tests of the selective precipitation of sulfate with barium carbonate now have been made and are reported herein.

TEST PLAN

In these tests, simulated scrubbing solutions of known composition first were prepared from the sulfates, sulfites, and bisulfites of sodium or potassium; then a measured amount of barium carbonate ($BaCO_3$) was added as a finely divided solid and the mixture was stirred continuously until the test had been completed (usually 3 hr). During the entire test, the solution was maintained at the desired test temperature. A timed series of samples was taken and filtered immediately. The solids were water washed, acetone washed, and air dried prior to infrared analysis to determine the proportions of $CO_3^=$, $SO_3^=$, and $SO_4^=$ present. The barium salts of these three anions have very low solubility. Precipitated proportions of the individual species of sulfur oxide and the residual $BaCO_3$ then were calculated from the infrared analysis and the input proportions. Data from the tests are given in Table 8 and in

TABLE 8. SELECTIVE PRECIPITATION OF SULFATE WITH BARIUM SALTS--TEST DATA

Test No.		1			2			3			4			5			6	
Soluble cation (X)		Na			Na			Na			Na			K			Na	
Input proportions, moles																		
X_2SO_4		1			-			-			1			1			1	
X_2SO_3		-			1			-			1			1			-	
$XHSO_3$		-			-			1			-			-			2	
$BaCO_3$		1			1			1			1			1			1.5	
$Ba:SO_4^=$ mole ratio		1			-			-			1			1			1.5	
Ba:S mole ratio		1			1			1			0.5			0.5			0.5	
Temperature, °C		52			49			52			49			49			52	
C_t		6.0			5.7			3.1			7.2			7.2			7.1	
C_a		0			5.7			3.1			3.6			3.6			3.5	
S_t		3.0			2.9			3.1			3.6			3.6			5.3	
S_a		0			2.9			3.1			1.8			1.8			3.5	
	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba
Results at time indicated																		
30 minutes																		
% of input S precipitated	57	-	-	-	51	-	5	52	-	21	7	-	9	10	-	15	7	-
% of individual ion precipitated	57	-	57	-	51	51	-	52	55	42	14	56	18	20	37	47	10	45
1 hour																		
% of input S precipitated	42	-	-	-	57	-	7	53	-	23	7	-	14	6	-	16	9	-
% of individual ion precipitated	42	-	42	-	57	57	-	53	60	46	14	60	29	12	41	48	13	50
3 hours																		
% of input S precipitated	51	-	-	-	71	-	8	71	-	26	9	-	16	9	-	17	11	-
% of individual ion precipitated	51	-	51	-	71	71	-	71	73	52	18	71	32	19	51	50	16	54

Test No.		7			8			9			10			11	
Soluble cation		Na			Na			Na			Na			Na	
Input proportions, moles															
X_2SO_4		1			1			1			0.1			0.1	
X_2SO_3		-			-			-			-			-	
$XHSO_3$		2			2			2			0.9			0.9	
$BaCO_3$		2			3			2			1			1	
$Ba:SO_4^=$ mole ratio		2			3			2			10			10	
Ba:S mole ratio		0.67			1			0.67			1			1	
Temperature, °C		52			52			49			52			77	
C_t		7.1			6.9			0.7			3.8			3.8	
C_a		3.5			3.4			0.4			3.1			3.1	
S_t		5.3			5.2			0.5			3.4			3.4	
S_a		3.5			3.4			0.4			3.1			3.1	
	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba	$SO_4^=$	$SO_3^=$	Ba
Results at time indicated															
30 minutes															
% of input S precipitated	21	12	-	32	34	-	16	13	-	16	36	-	7	67	-
% of individual ion precipitated	63	18	58	95	51	66	48	19	44	160	40	52	70	74	75
1 hour															
% of input S precipitated	23	13	-	32	33	-	16	16	-	14	48	-	8	67	-
% of individual ion precipitated	70	19	53	97	50	66	48	24	48	140	53	52	80	74	75
3 hours															
% of input S precipitated	23	21	-	30	44	-	19[a]	18[a]	-	9	66	-	9	70	-
% of individual ion precipitated	69	31	65	90	66	74	57[a]	27[a]	56[a]	90	73	75	90	78	80

[a] Test duration, 2-1/2 hours.

Figures 14 through 24. Only a portion of the data are given in the table; the portion given was selected to illustrate the rate and degree of completion of the reactions. More complete data are given in the figures.

In the table and figures, the expressions C_t, C_a, S_t, and S_a represent the moles of sodium (or potassium) or of sulfur per 100 moles of total water. The "C" values are moles of cation and the "S" values are moles of sulfur. Subscript "t" indicates total ion present; subscript "a" indicates active ion present (sulfite or cation associated with the sulfite). Total water includes free water plus 1/2 mole per mole of bisulfite.

EVALUATION OF DATA

Tests 1, 2, and 3 were made with solutions of the individual salts, sodium sulfate, sulfite, and bisulfite, to which the stoichiometric amount of $BaCO_3$ was added to determine the rate and extent of the reaction in each system. In these tests S_t and the temperature were held at the same levels, 3 moles per 100 moles of water and 49° to 52°C, respectively. Sulfite and bisulfite reacted about equally rapidly and to the same degree, reaching about 50% in 1 hour and 70% in 3 hours; sulfate reacted more slowly, the values being only 40 and 50%, respectively. This comparison would indicate that the sulfate is not preferentially precipitated.

Test 4 was made with a mixture of sulfate and sulfite, with a slightly higher S_t (3.6) than in tests 1, 2, and 3, but with half the sulfur in sulfite form ($S_a = 1.8$). Only enough $BaCO_3$ was added to react with half the sulfur; thus the preferential reaction, if it existed, could be demonstrated. Preferential precipitation of sulfate was shown in each sample; sulfate precipitation was about three times sulfite precipitation. Only about 70% of the barium was utilized, as in tests 2 and 3, probably indicating some blinding of the $BaCO_3$.

Test 5 was made at the same conditions as test 4 except that potassium salts were substituted for the sodium sulfate and sulfite. During the initial 15-minute period, sulfate was preferentially precipitated; at 30 minutes, sulfate and sulfite precipitation were about equal. After 1 hour and 3 hours, however, there was a 2:1 preference for sulfate exhibited. The reaction with potassium salts was preferential with the sulfate, but not to the extent exhibited in the sodium system.

In tests 6, 7, and 8, mixtures of 1 mole sodium sulfate and 2 moles sodium bisulfite, dissolved and diluted to an S_t of 5.3 and an S_a of 3.5, were mixed with amounts of $BaCO_3$ to result in input stoichiometries (Ba:S mole ratios) of 0.5, 0.67, and 1.0, respectively. The temperature was held at 52°C. In test 6 (Ba:S = 0.5), the precipitate contained about two-thirds of its sulfur in sulfate form even though the solution contained two-thirds in sulfite form. Of the individual species, about three times as great a proportion of the sulfate was precipitated (50% at 3 hr) as was the sulfite (16% at 3 hr). Total barium utilization was only 54% at 3 hours.

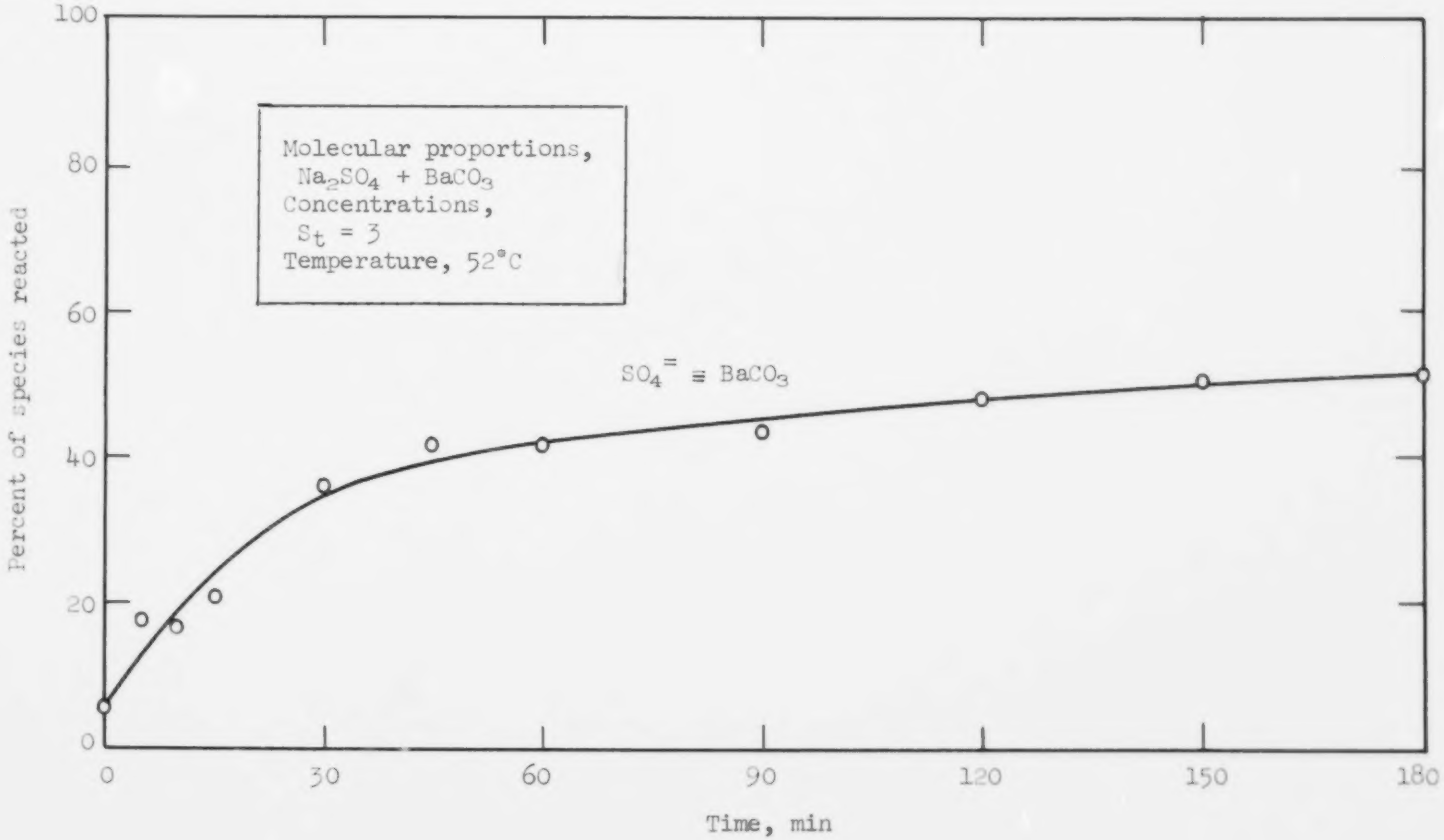


Figure 14. Laboratory precipitation of sulfate with barium carbonate--test 1.

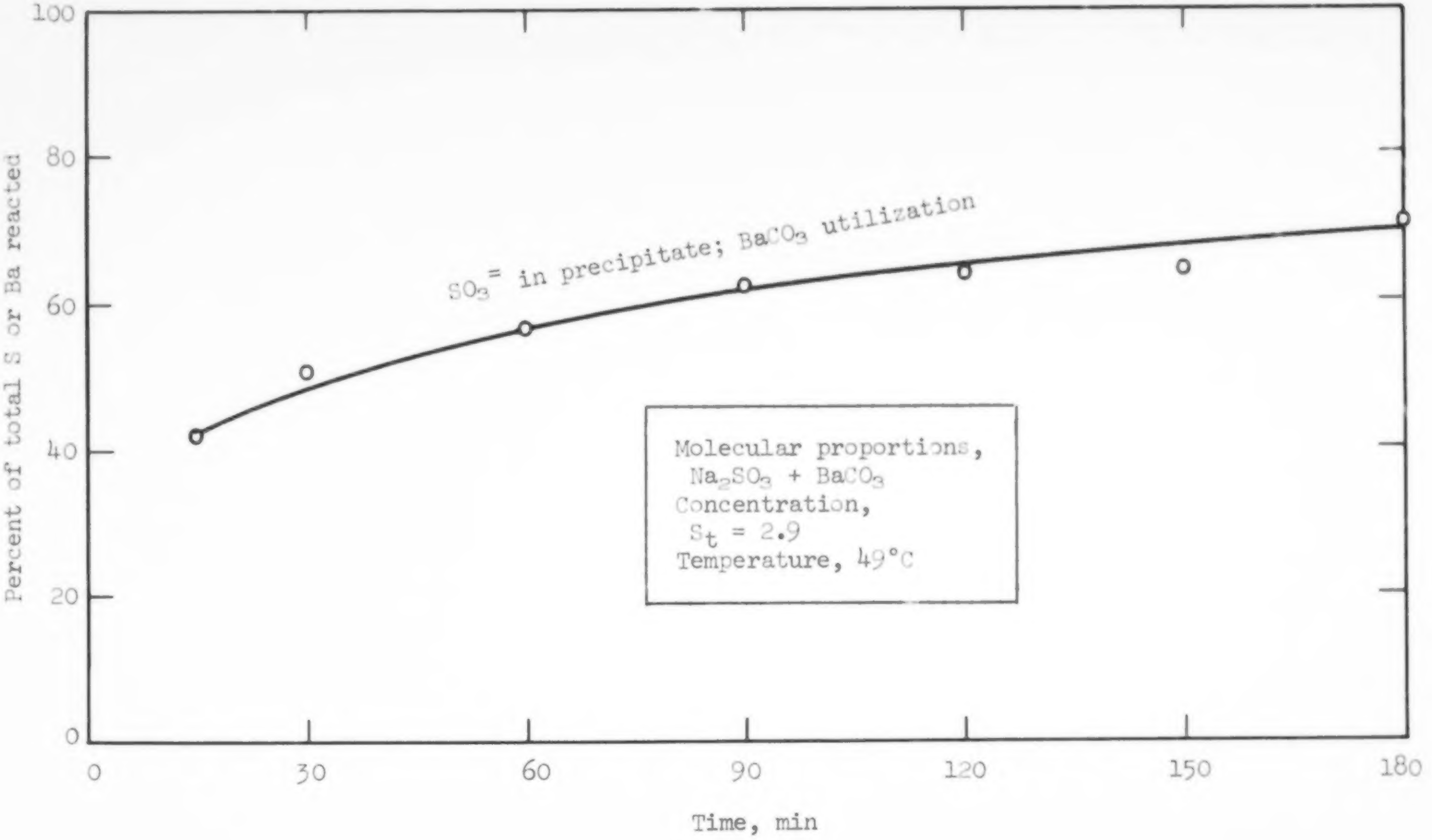


Figure 15. Laboratory precipitation of sulfite with barium carbonate--test 2.

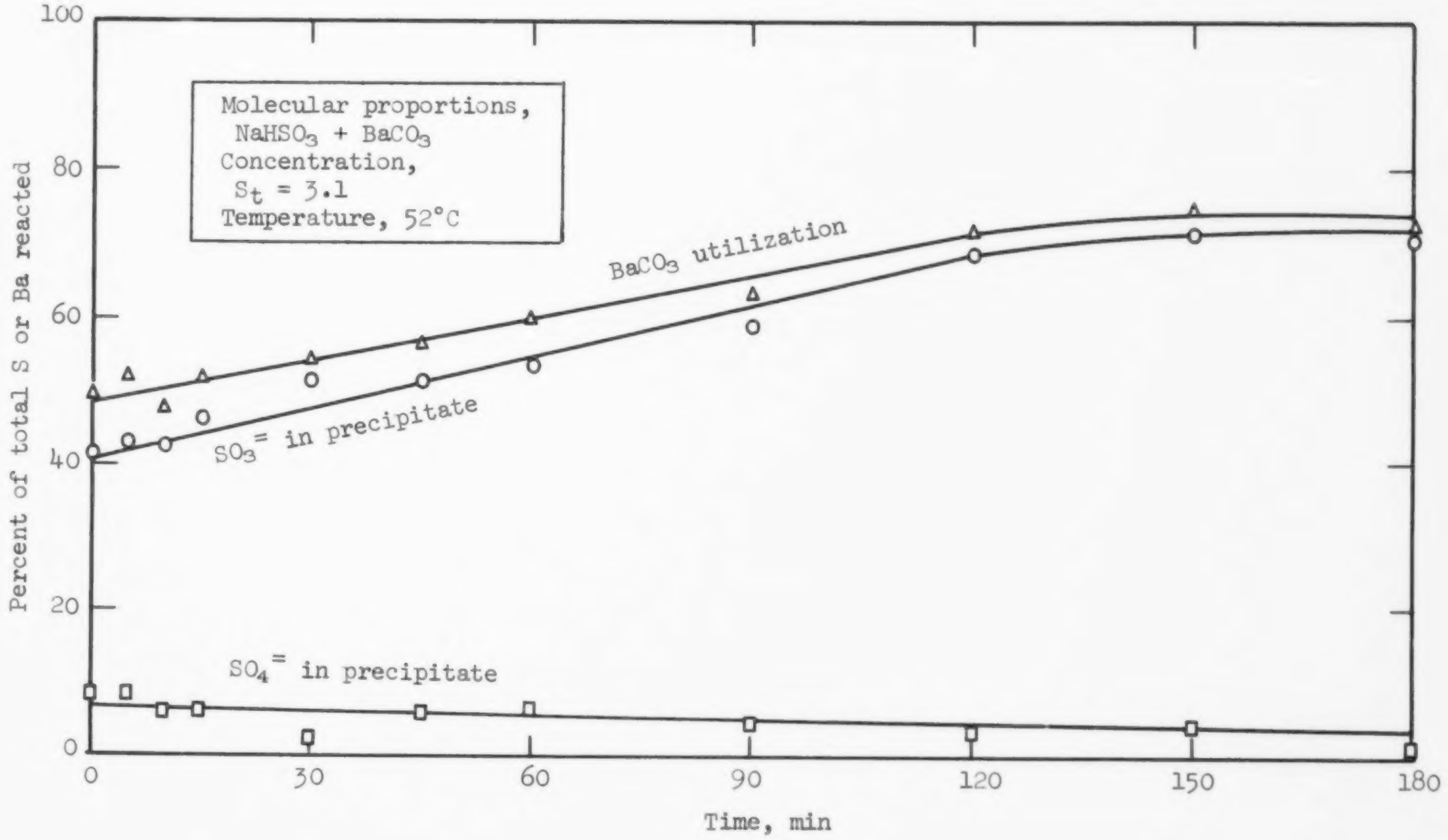


Figure 16. Laboratory precipitation of sulfite with barium carbonate--test 3.

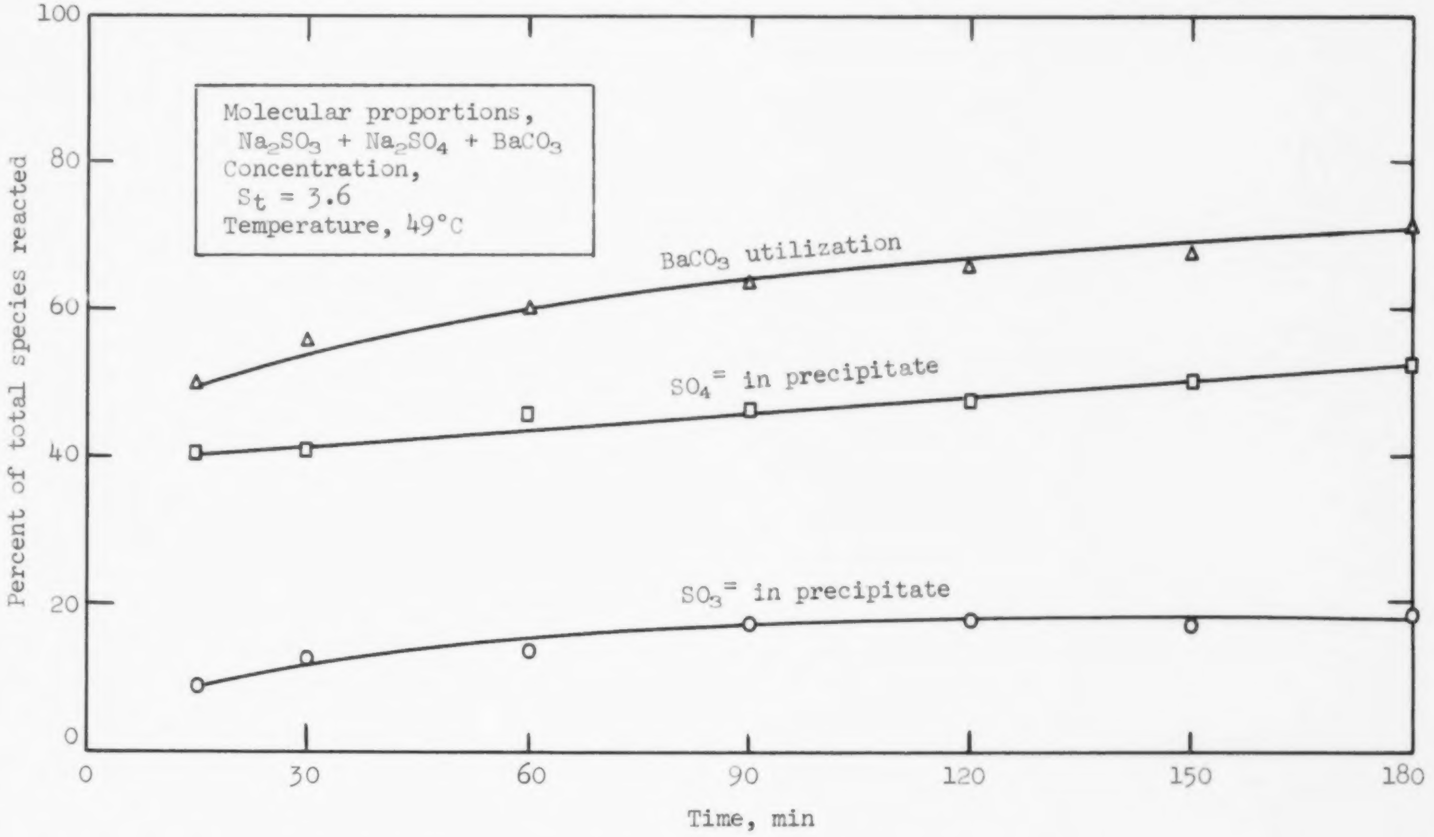


Figure 17. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 4.

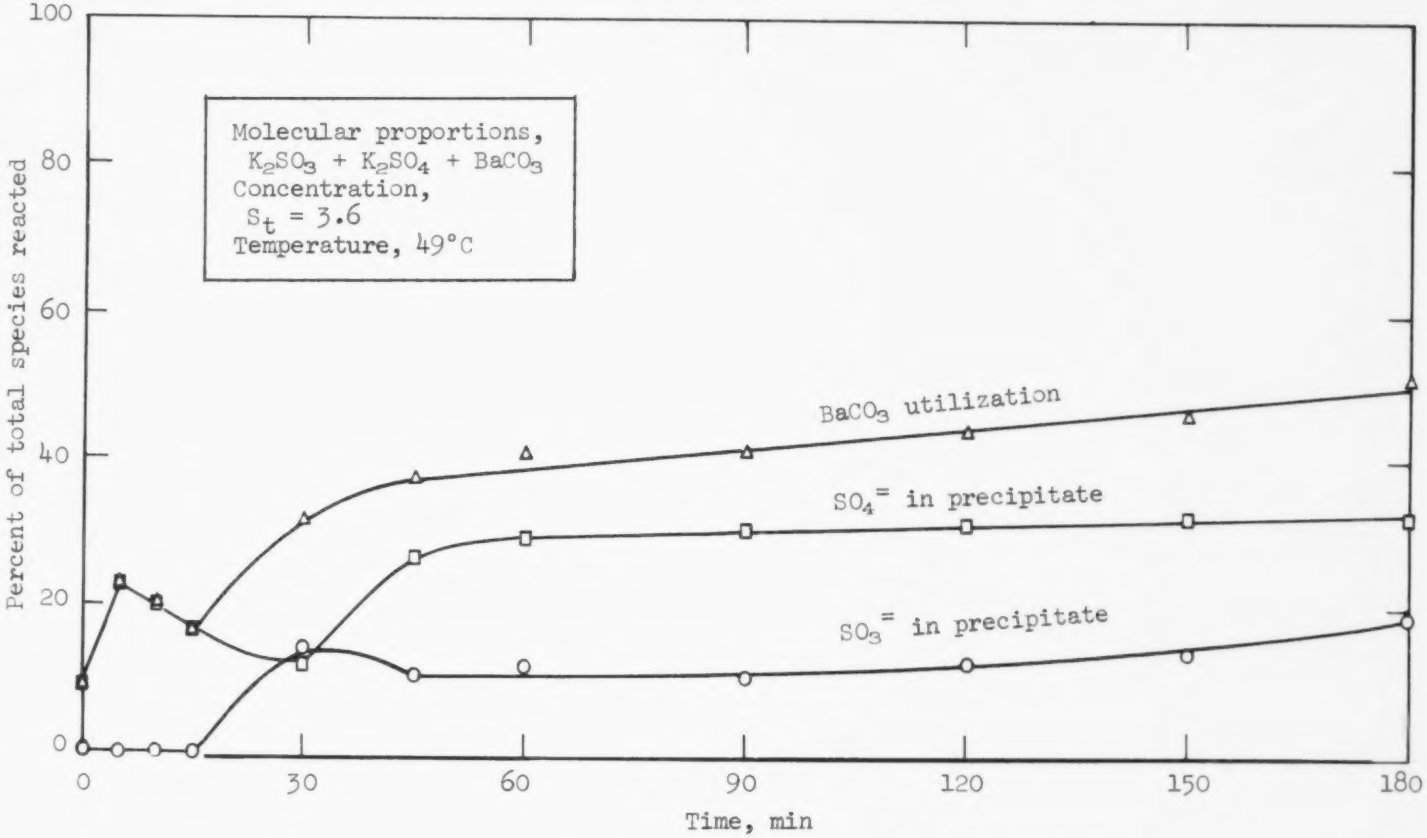


Figure 18. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 5.

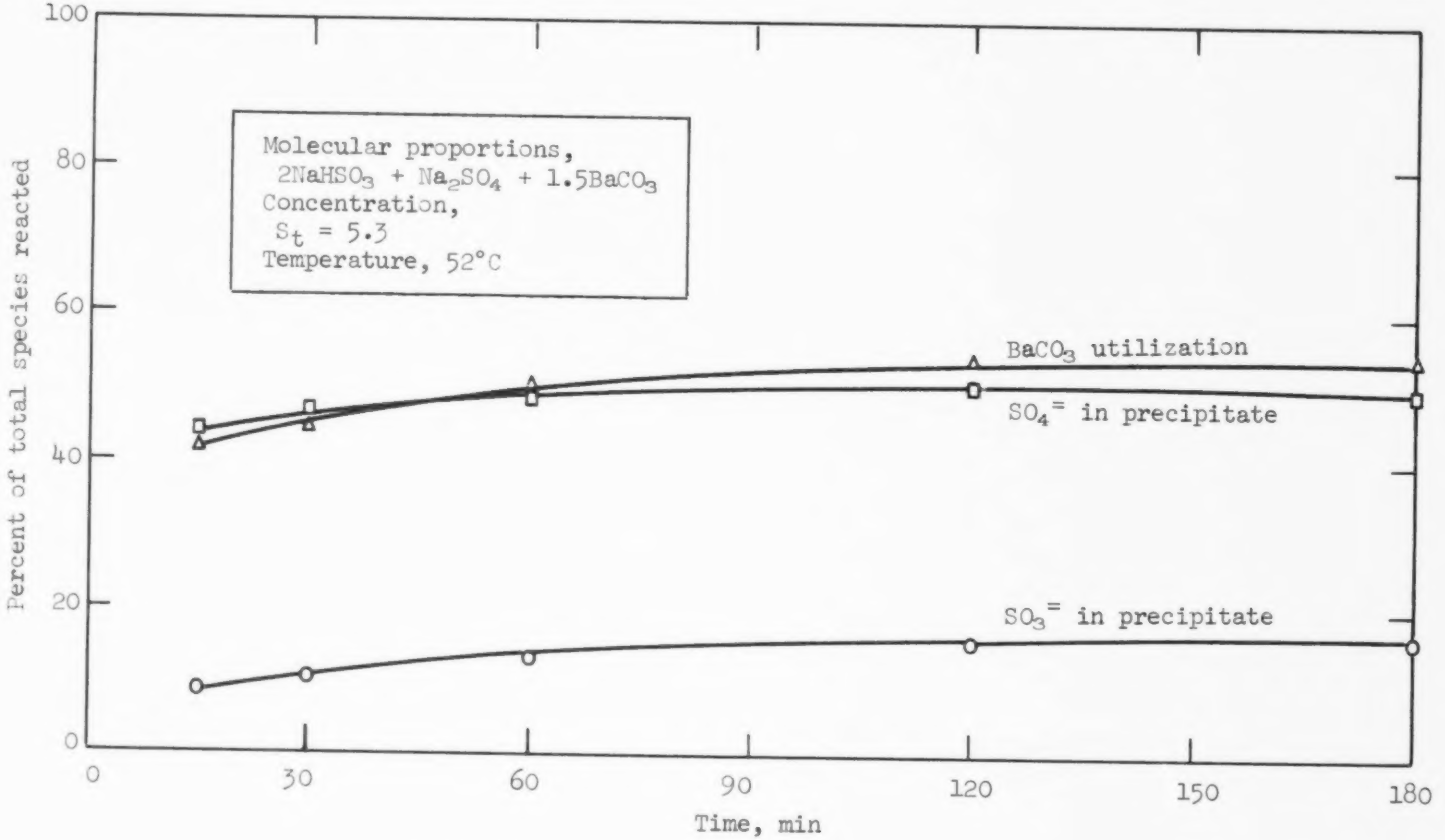


Figure 19. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 6.

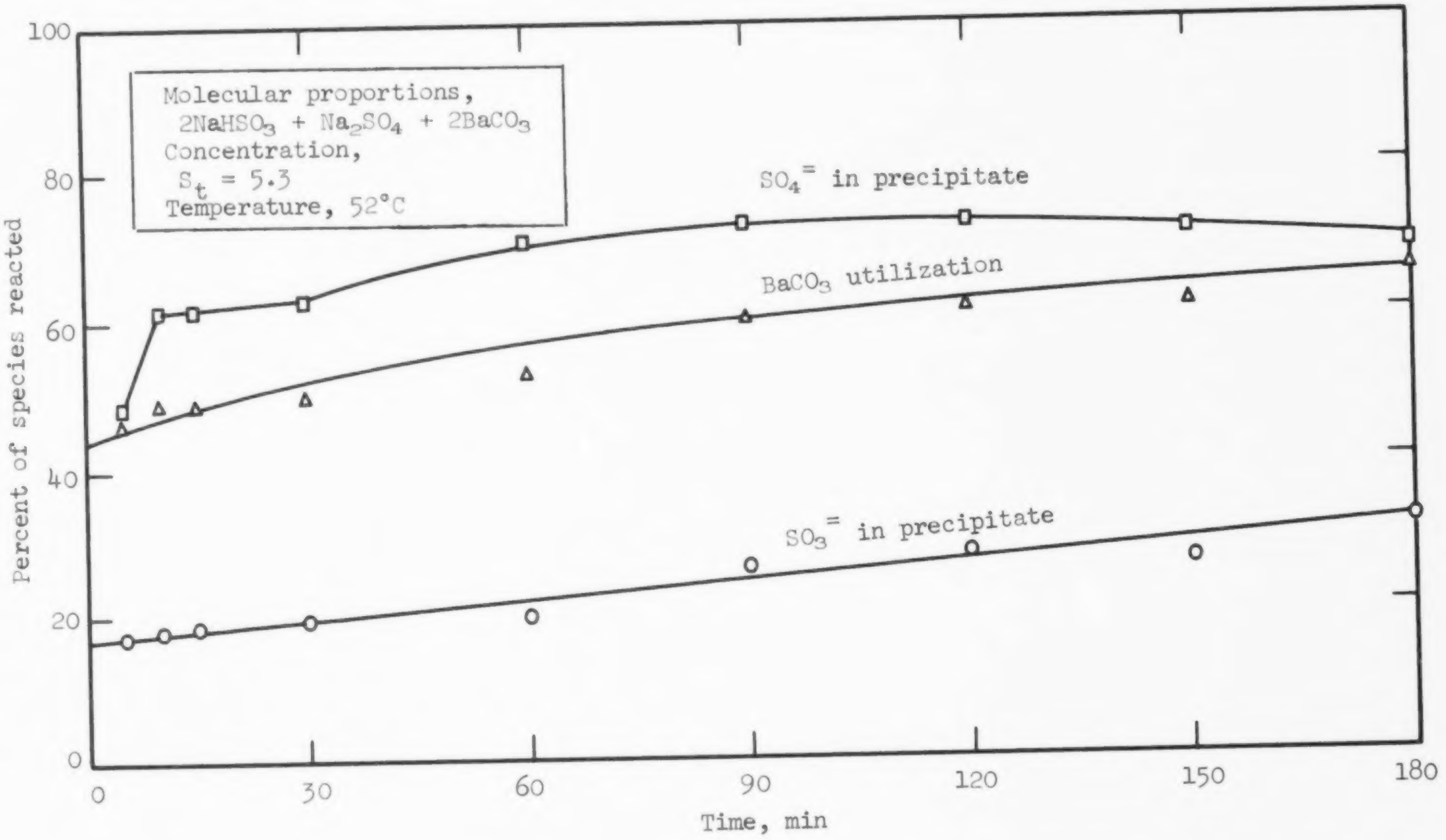


Figure 20. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 7.

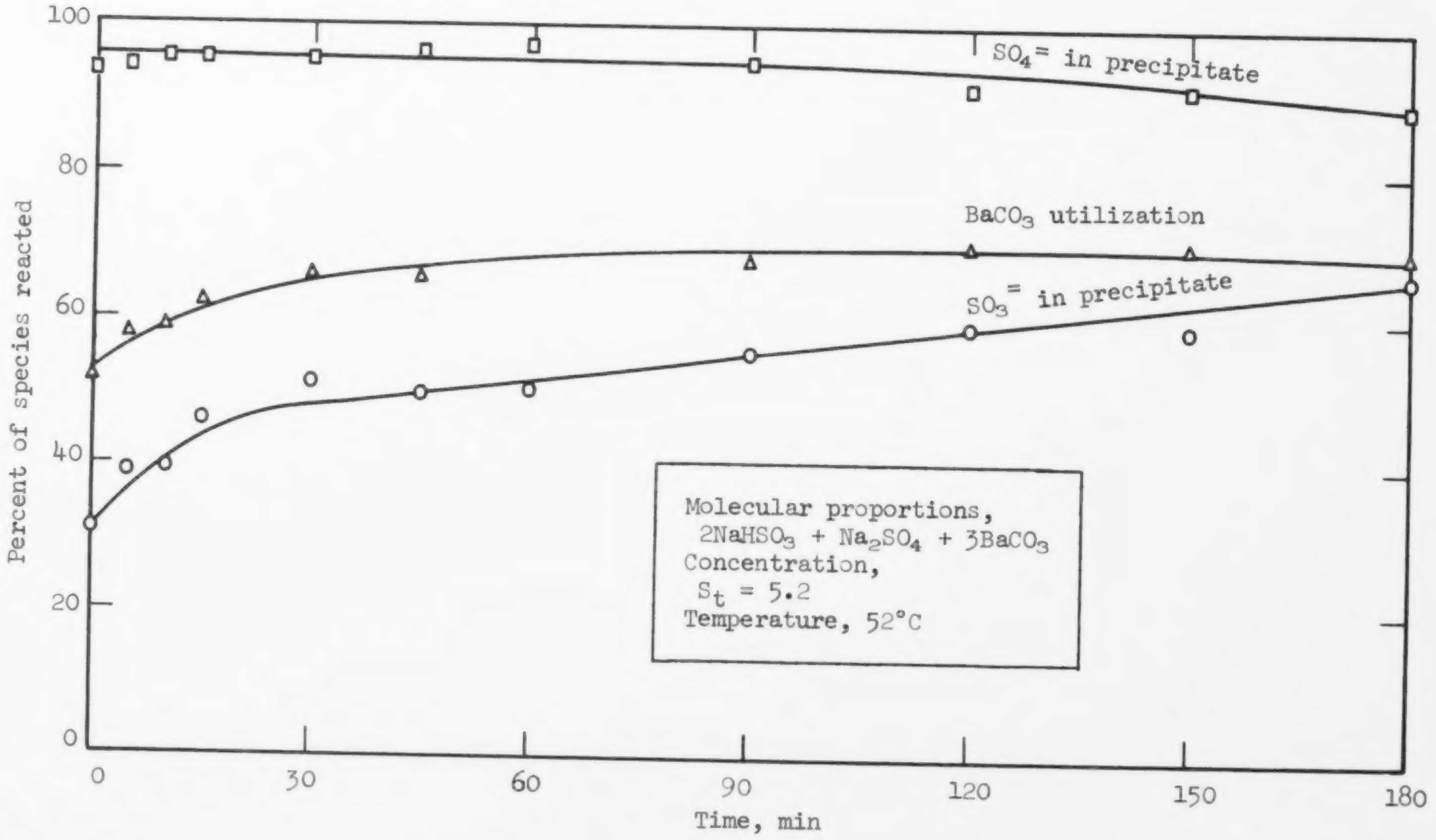


Figure 21. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 8.

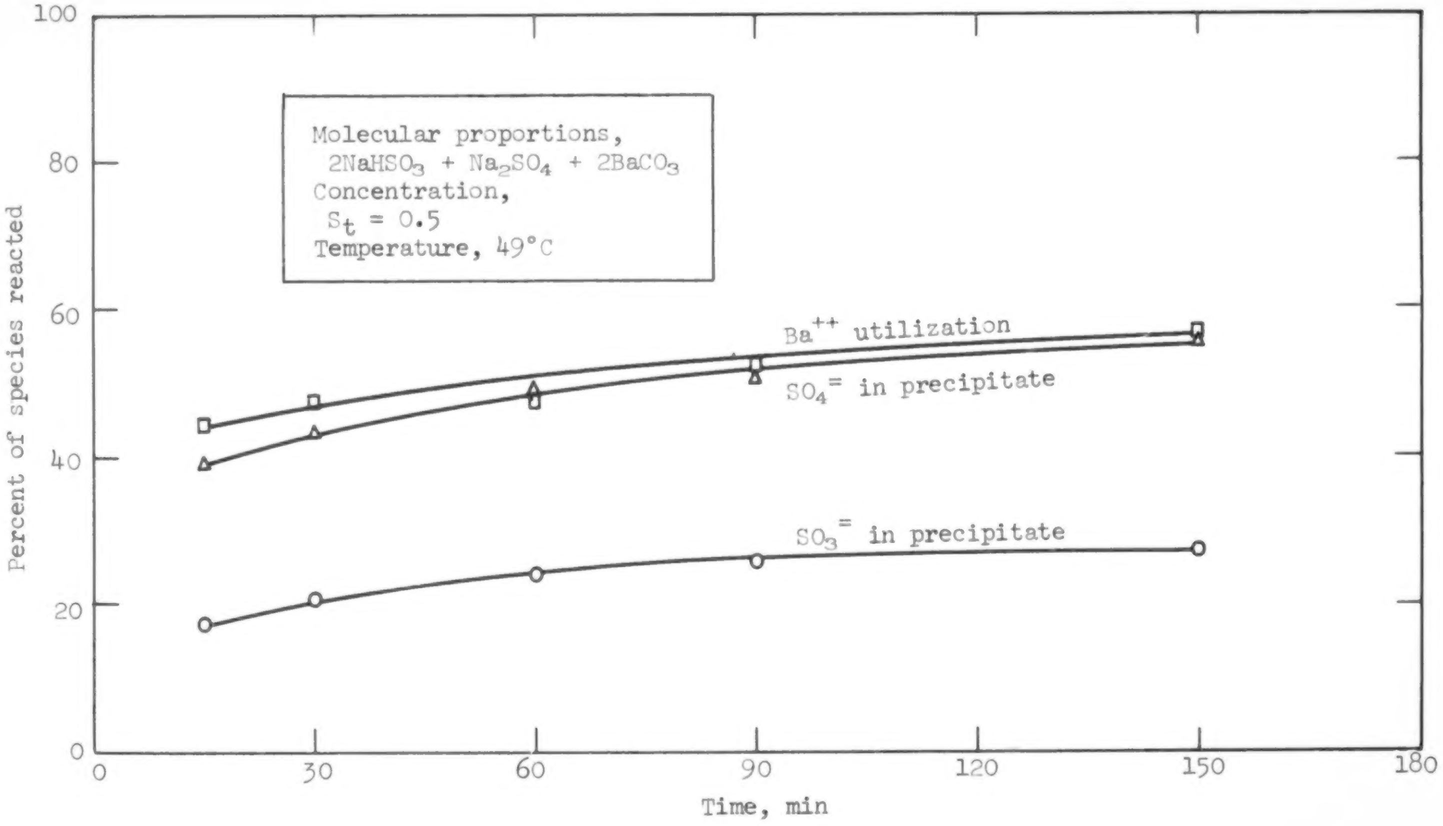


Figure 22. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 9.

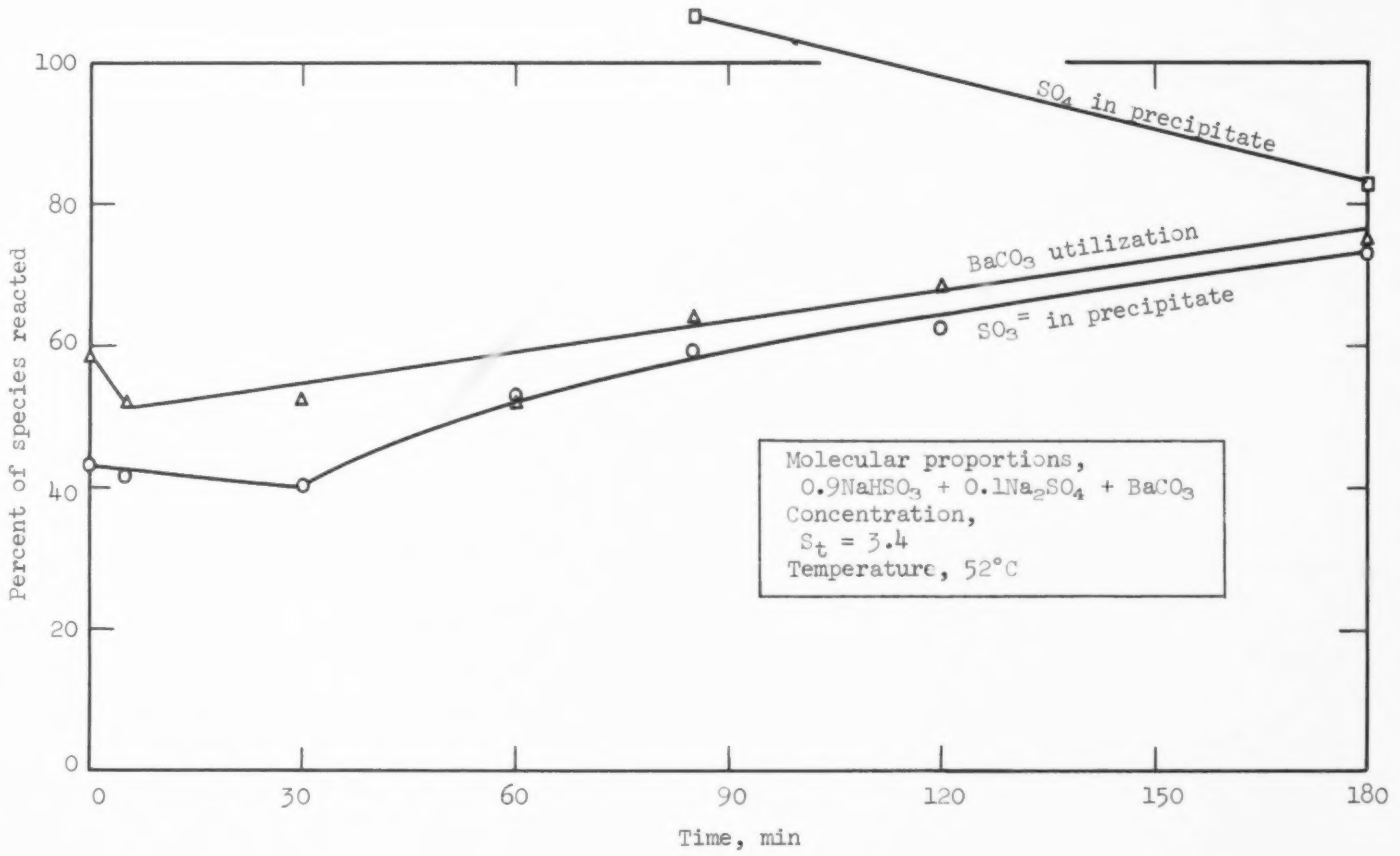


Figure 23. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 10.

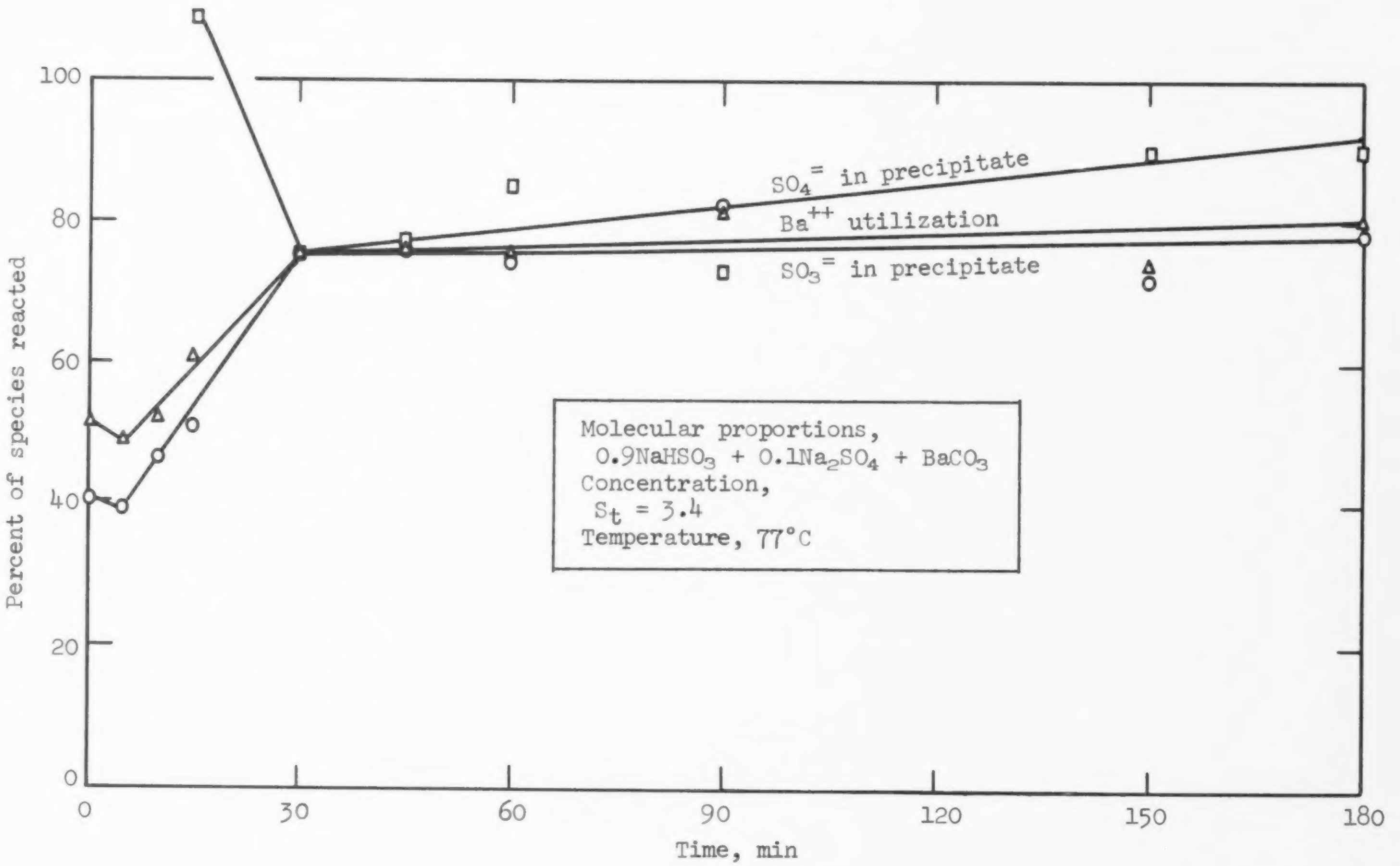


Figure 24. Laboratory precipitation of sulfate and sulfite with barium carbonate--test 11.

Increasing the proportion of $BaCO_3$ in test 7 to Ba:S mole ratio of 0.67 resulted in an early (30 min and 1 hr) precipitation of about three times greater proportion of the sulfate than of the sulfite. These were about the same proportions as precipitated in test 6. After 3 hours, however, the preference was less noted and the proportion of the sulfate precipitated was only twice that of the sulfite. Final $BaCO_3$ utilization was 65%. Final sulfate precipitation was 69% of that present.

A further increase of $BaCO_3$ proportion to a Ba:S mole ratio of 1 in test 8 resulted in a furtherance of the trend seen in test 7 compared with test 6. The final proportion of sulfate precipitated was about 1-1/2 times that of the sulfite, and $BaCO_3$ utilization increased to 70%. After 3 hours, 90% of the sulfate had been precipitated.

Test 9 was the same as test 7 except that the system was diluted from an S_t of 5.3 to a less practical S_t of 0.5, a tenfold dilution; and the test was carried out for only 2-1/2 hours instead of 3 hours. Results at 30 minutes indicated that a 2-1/2 times greater proportion of sulfate was precipitated than of the sulfite. Thereafter, the preference was reduced to about twofold. Final results were very similar to those of test 7; the final sample contained about twice the proportion of the sulfate in precipitated form as it did the sulfite (57% vs. 27%) and $BaCO_3$ utilization was about 60%.

In regenerative systems the sulfate will build, unless controlled, until the physical losses from the system remove sulfate at the rate it is being formed. Sulfate sulfur could, conceivably, reach 90% or more of the total sulfur present. In nonregenerative systems, however, sulfate level would be much less. Tests 10 and 11 were made with proportions of sulfate and bisulfite at about the levels expected in the effluent of a nonregenerative scrubber system on a conventional coal-fired boiler; about 10% of the sulfur was in sulfate form. The S_t was held at 3.4. Enough $BaCO_3$ was added to provide the stoichiometric requirement of all the sulfur. The differences in the tests were the temperatures at which the reaction was carried out, 52°C in test 10 and 77°C in test 11. The different temperatures were tested because the solubility relationship of barium sulfite ($BaSO_3$) to barium sulfate ($BaSO_4$) is reported to reverse at and above the higher temperature. Early (30 min and 1 hr) results from test 10 indicated precipitation of more sulfate than existed in the sample. This may have been due to the low sulfate proportion and to incomplete drying of these samples. However, the sulfate to sulfite ratio probably is correct and the results show that a four times greater proportion of the sulfate than the sulfite was precipitated at 30 minutes. By 1 hour, the proportion was only about three times greater and at 3 hours the proportion was reduced to about 1.25. About 75% of the $BaCO_3$ was utilized. Test 11 results, although about the same after 3 hours, were quite different during the early part of the test when the proportions of sulfate and sulfite precipitated were almost equal at 30 minutes and 1 hour. This would support the fact that at 77°C the solubilities of $BaSO_4$ and $BaSO_3$ are more nearly equal than at 52°C at which temperature $BaSO_4$ is the least soluble.

CONCLUSIONS

These tests show the selective precipitation of sulfate from a solution of sodium sulfate and sodium sulfites by the addition of $BaCO_3$. In tests where the addition of $BaCO_3$ was 1 to 1.5 times the equivalent of the sulfate content of the solution and the temperature was held at 52°C or lower (tests 4 and 6), sulfate precipitation was more selective than in tests at similar conditions and higher $BaCO_3$ ratios (tests 8 and 10). Test results indicate that the sodium system might be more amenable to selective sulfate precipitation by this means than would be the potassium system. It is concluded that selective precipitation of sulfates by reaction with $BaCO_3$ is a technically feasible means of removing soluble sulfates from regenerative scrubbing systems and thereby obviating problems associated with sulfate buildup. The selectivity of sulfate precipitation by barium is important since other cations, such as calcium, are very selective in precipitating sulfite. Any sulfite precipitated with sulfate is undesirable but not so much so as to make the process unviable; it would mean that a larger charge of material would need to be subjected to the reduction, hydrolysis, and carbonation steps, however. Low barium utilization would add to this load also. Barium carbonate is poisonous when taken by mouth and this might be a deterrent to its use; barium sulfate is a nontoxic, insoluble salt.

UTILIZATION OF WEAK SULFURIC ACID PRODUCED IN POLLUTION CONTROL PROCESSES

Several sulfur dioxide (SO_2) scrubbing processes have been tested from which a product stream of sulfuric acid is recovered. Some of the more direct of these processes depend on the following sequence: (1) adsorption of SO_2 from a dilute gas stream in a bed of activated carbon, (2) oxidation of the SO_2 to SO_3 by the oxygen present in the gas, (3) hydration to the acid form, and (4) removal of the product sulfuric acid from the carbon by elutriation with water; the "Sulfacid" process (6) is an example. The processes differ, primarily, in the means of separating the steps of the procedure. Some processes also include a sulfuric acid concentration step which utilizes heat in the gas stream for the purpose. The concentration of the sulfuric acid produced varies with the design of the process, with the concentration of SO_2 in the waste gas, and with the degree of SO_2 recovery attained. Generally, sulfuric acid concentration may vary over the range 5 to 30%. Sulfuric acid purity may vary as a result of its contact with impurities from the gas stream; impurities may include any of the materials in the fly ash, the amount being, generally, a function of the degree to which the fly ash is removed prior to the SO_2 removal step. The most common and most concentrated of the dissolved contaminants probably are calcium and iron sulfates.

In order for such an SO_2 removal process to be viable, some use must be made of the weak sulfuric acid. In Japan, some plants simply neutralize the acid with lime or limestone and produce gypsum which then is used in production of the construction materials, cement and wallboard. Such practice does not appear feasible on a large scale within the United States because of the competition of natural gypsum and the production processes already installed to utilize that material. There is an experimental installation to make gypsum from dilute sulfuric acid in Florida (7), however.

Other uses of weak sulfuric acid might be found. For example, at about 15% concentration, it is used in pickling metal surfaces, and at other concentrations it might be used for water treatment, pH control, etc. A major power plant installation of such a process would, however, produce so much sulfuric acid that a large portion might have to be transported over long distances for disposition. A 500-MW power plant burning 3.5% sulfur coal would produce about 5000 tons of 10% sulfuric acid per day. The corrosiveness of the weak acid, compared with that of the highly concentrated product (> 90%) usually shipped, would add to the problems and cost of transport. A method of utilization or concentration of the acid at or near the power plant site is needed.

Concentration of the acid from the 500-MW plant, above, from 10 to 92% would require the removal of about 185.7 tons of water per hour; if this were done by heating, the energy required for evaporation alone would be about 92 million kilogram-calories (364 million Btu) per hour. This is equivalent to 106 MW or about 20% of the power output of the plant.

Some method of utilization of weak sulfuric acid is needed that will reduce the energy requirement for removal of water from either the acid or its product. Methods under consideration include the following:

1. React weak sulfuric acid with melamine to produce solid melamine sulfate; remove solid by filtration or decantation; neutralize with ammonium, potassium, or sodium hydroxide (or carbonate); wash the sulfate salt from the melamine as a solution more concentrated than would be possible from the original acid and process it to the dry salt; and recycle the melamine.

2. Utilize the weak sulfuric acid to extract phosphate rock and subject the product phosphoric acid to the same procedure as in item 1. Such a process should produce phosphate salts of very low impurity content and might allow formation of clear liquids from acid produced from uncalcined Florida phosphate rock.

3. Remove water from the weak sulfuric acid, the product phosphoric acid (item 2), or from one of the salt solutions from the melamine separation and neutralization steps (items 1 and 2) by freeze drying or concentration instead of normal evaporative drying methods. The energy requirements might be much less if freeze concentration were employed.

Some work has been done in which freeze concentration of phosphoric acid and of ammonium phosphate solutions have been tested. Results are reported later. In other work, reported below, weak sulfuric acid has been used to extract phosphate rock to produce phosphoric acid.

USE OF WEAK SULFURIC ACID FOR EXTRACTION OF PHOSPHATE ROCK

Test Plan and Equipment

A factorial experiment was carried out for study of the extraction of phosphate rock with weak sulfuric acid; its parameters are shown below.

Variable	Level -	 +
A - Rock particle size	Coarse	Fine
B - Reaction temperature, °C	24	52
C - Sulfuric acid concentration, %	10	30
D - Acid addition time, hr	1	2

The full test plan is shown in Table 9.

TABLE 9. EXTRACTION OF PHOSPHATE ROCK WITH WEAK SULFURIC ACID--TEST PLAN

		Variable			
Test position	Test No.	A, rock grind[a]	B, temperature, °C	C, H_2SO_4 concentration, %[b]	D, acidulation time, hr
1	2	Coarse	24	10	1
2	5	Coarse	24	10	2
3	15A	Coarse	24	30	1
4	10	Coarse	24	30	2
5	4	Coarse	52	10	1
6	6	Coarse	52	10	2
7	14	Coarse	52	30	1
8	9A	Coarse	52	30	2
9	3	Fine	24	10	1
10	8	Fine	24	10	2
11	16	Fine	24	30	1
12	12	Fine	24	30	2
13	1A	Fine	52	10	1
14	7	Fine	52	10	2
15	13	Fine	52	30	1
16	11	Fine	52	30	2

---

[a]

	Screen analysis, mesh, of rock, %						
	-10 +20	-20 +35	-35 +50	-50 +100	-100 +200	-200 +325	-325
Coarse	15.6	41.5	16.1	20.9	3.5	0.5	1.9
Fine	-	-	< 0.1	0.35	10.85	23.8	65.0

	Chemical analysis of rock, %						
	CaO	MgO	Fe_2O_3	Al_2O_3	F	P_2O_5	SO_3
Coarse	47.1	0.24	1.5	1.9	3.7	32.8	0.7
Fine	46.0	0.38	1.4	1.1	3.7	30.6	0.1

[b] Actual concentrations: 9.23% and 27.3% H_2SO_4.

Prior to making the batch tests, calculations were made of the maximum phosphoric acid concentration that could be expected from each concentration of sulfuric acid and the grade of phosphate rock in use. The rock (100 g) was prewet in a 9.5-centimeter-diameter (3.75-in-dia) glass vessel 25 centimeters (10 in) high with 130 grams of phosphoric acid of the calculated concentration and was held at test temperature for a period of 30 minutes; this is the approximate amount of acid that would be available for recycle if the cake were washed countercurrently with 1.3 grams of water per gram of rock. At the end of the prewet period, feed of sulfuric acid to the prewet rock was begun. The acid was fed from a constant-head feeder (Mariotte's bottle) with the tip of the delivery line touching the moving slurry surface; this tended to eliminate dripping and allowed for more nearly continuous feed, particularly when feeding the stronger acid over the longer time. Agitation was maintained, using a 7.6-centimeter-diameter (3-in-dia), two-blade propeller-type agitator, at a constant rate (280 rpm) throughout the prewet, acidulation, and a 15-minute postacidulation period. The product slurry was transferred immediately to a stainless steel filter frame with a square 8.33-centimeter (3.281-in) 100-mesh stainless steel screen [69.5 cm^2 (10.767 in^2)] as the filter medium. Filtrations were timed to the first appearance of solid cake above the fluid surface. Vacuum was maintained at 38 centimeters mercury (±0.75 cm Hg) by installation of a vacuum surge tank and a vacuum control valve on the laboratory vacuum system. A plug cock mounted on the filter drain served to apply and to isolate suction rapidly and as required. Both the volume and the weight of the filtrates were measured. The filter cake, typically 1.25 centimeters (1/2 in) thick, was allowed to dewater after the second wash by continued application of vacuum until no more liquid ran from the filter and then was transferred as quantitatively as possible to trays for oven drying to essentially constant weight at 57°C (the temperature was limited to prevent dehydration of the gypsum); both wet and dry weights of the cakes were recorded. The dried filter cake, product acid filtrate, and both wash solutions were submitted to the general analytical laboratory for analysis. The data collected are given in Table 10.

Evaluation of Data

Evaluation was made of the responses measured and of calculations made from those responses. Calculated values included those to show the proportions of the rock constituents in the acid and the proportions and forms of P_2O_5 in the filter cake. Also calculated were the filtration rates expressed as kilograms of rock, kilograms of P_2O_5, and cubic meters of liquid per hour per square meter of filter area. Filtration rates were calculated for the initial (product acid) filtration step alone and for the total process including both wash steps. The calculated responses are given in Table 11. The statistical analysis of these responses is given in Table 12.

The statistical analysis shows the average of each calculated response and the difference in response due to each variable. Also shown are the averages and differences for the interactions of each pair of variables. The three- and four-variable interactions were considered to be highly unlikely and were considered to be error; the error in the data thus was calculated from the differences in the averages of the three- and four-variable interactions. From the error, so calculated, the values of the least

TABLE 10. EXTRACTION OF PHOSPHATE ROCK WITH WEAK SULFURIC ACID--PRIMARY DATA

	Test position															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Filtration time, sec																
Product acid	138	147	107	66	46	50	24	34	60	58	61	68	52	64	25	19
First wash	45	52	136	133	18	24	70	158	17	16	89	141	18	26	65	53
Second wash	45	52	93	91	23	28	63	107	16	17	65	104	18	33	47	55
Total	228	251	336	290	87	102	157	299	93	91	215	313	88	123	137	127
Filtrate volume, ml																
Product acid	685	700	186	116	697	640	91	66	815	810	136	109	820	810	94	84
First wash	134	144	138	132	154	176	150	120	126	127	134	136	122	125	144	132
Second wash	191	207	175	182	195	210	174	196	202	204	165	167	192	190	169	175
Total	1010	1051	499	430	1133	1026	415	382	1143	1141	435	412	1134	1125	407	391
Filtrate weight, g																
Product acid	704	723	213	133	721	658	106	77	847	838	156	125	846	835	107	96
First wash	136	150	156	152	160	184	173	138	130	132	151	154	126	128	164	150
Second wash	191	209	178	190	198	212	183	209	201	203	174	177	193	189	178	186
Total	1031	1082	547	475	1079	1054	462	424	1178	1173	481	456	1165	1152	449	432
Dry cake weight, g	135.9	139.6	132.4	153.1	140.3	140.6	141.2	132.9	140.7	141.6	146.6	151.1	142.3	141.8	142.0	138.7
Chemical analysis, %																
Dry cake																
CaO	32.5	31.6	33.1	30.5	31.6	31.2	31.3	31.0	30.8	30.3	30.3	29.9	30.5	31.0	30.3	27.9
P_2O_5																
Total	4.56	2.75	7.50	4.34	2.05	1.60	2.40	2.57	1.96	2.05	3.13	2.55	1.92	2.10	2.01	1.85
N.A.C. insoluble[a]	2.70	1.56	4.91	1.50	1.02	0.54	0.38	0.56	0.33	0.25	0.07	0.05	0.24	0.29	0.17	0.17
Water soluble	0.40	0.39	1.14	1.45	0.32	0.37	1.38	1.33	0.62	0.69	1.31	1.44	0.57	0.57	1.33	1.29
A.C. soluble[b]	0.64	0.71	0.70	1.55	0.62	0.71	1.49	1.11	1.32	1.51	1.91	1.94	1.38	1.49	1.29	0.92
SO_3	37.4	36.1	34.0	37.0	40.6	41.5	39.5	39.4	40.7	39.1	37.8	38.2	39.9	40.6	39.3	37.7
Product acid																
CaO	0.09	0.10	0.08	0.08	0.12	0.12	0.10	0.11	0.12	0.12	0.10	0.09	0.12	0.13	0.10	0.10
MgO	0.02	0.02	0.04	0.05	0.02	0.03	0.06	0.06	0.04	0.04	0.09	0.09	0.04	0.04	0.10	0.10
Fe_2O_3	0.04	0.04	0.11	0.15	0.06	0.06	0.25	0.29	0.05	0.05	0.14	0.15	0.06	0.06	0.24	0.28
Al_2O_3	0.07	0.08	0.22	0.26	0.13	0.15	0.39	0.40	0.04	0.05	0.14	0.04	0.06	0.07	0.20	0.22
F	0.25	0.30	0.54	0.70	0.34	0.35	0.89	0.90	0.33	0.33	0.80	0.50	0.34	0.36	0.93	0.92
P_2O_5	3.44	3.49	10.7	12.0	3.70	3.80	13.4	13.9	3.45	3.44	12.1	12.4	3.52	3.52	13.3	13.5
SO_3	1.25	1.18	5.76	3.74	1.05	0.91	2.54	2.64	0.92	0.96	2.67	2.67	0.93	0.98	2.15	2.40
First wash																
CaO	0.12	0.12	0.08	0.08	0.15	0.15	0.11	0.12	0.14	0.15	0.12	0.09	0.15	0.14	0.12	0.12
P_2O_5	3.60	3.60	9.92	12.12	3.78	3.93	13.82	14.13	2.94	3.04	12.25	12.64	2.67	2.70	13.62	12.73
Second wash																
CaO	0.12	0.11	0.09	0.10	0.14	0.13	0.13	0.13	0.10	0.10	0.13	0.10	0.09	0.09	0.15	0.13
P_2O_5	1.03	1.69	2.07	5.24	1.43	1.71	5.37	6.97	0.06	0.09	4.59	6.02	0.07	0.07	5.51	6.91

[a] N.A.C. = neutral ammonium citrate insoluble (A.O.A.C. method).
[b] A.C. = alkaline citrate soluble (exclusive of water soluble).

TABLE 11. EXTRACTION OF PHOSPHATE ROCK WITH WEAK SULFURIC ACID--CALCULATED RESPONSES

Response calculated	Overall average	Test position															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Filtration rates																	
Product acid																	
Kg rock/(hr)(m^2)	1114	375.5	352.5	484.3	785.1	1126.9	1036.5	2159.5	1523.8	863.7	893.5	849.5	762.2	996.5	810.0	2073.1	2727.9
m^3 acid/(hr)(m^2)	3.7	2.57	2.47	0.90	0.91	7.85	6.63	1.96	1.01	7.04	7.24	1.16	0.83	8.17	6.56	1.95	2.29
Kg rock P_2O_5/(hr)(m^2)	352	123.0	115.7	158.7	257.8	369.6	339.8	708.5	500.0	264.1	273.4	259.7	233.4	305.2	248.0	634.2	834.9
Total filtrate																	
Kg rock/(hr)(m^2)	357	227.5	206.5	154.3	178.7	595.7	508.3	330.1	173.3	557.1	569.3	241.2	165.5	588.8	421.4	378.4	408.2
m^3 acid/(hr)(m^2)	3.1	2.29	2.17	0.77	0.77	6.75	5.21	1.37	0.66	6.37	6.50	1.05	0.68	6.68	4.74	1.54	1.60
Chemical responses																	
Rock components in cake, %																	
CaO	93.62	93.77	93.66	93.05	99.14	94.13	93.14	93.83	87.47	94.21	93.27	96.56	98.22	94.35	95.56	93.53	84.12
P_2O_5																	
Total	12.50	18.89	11.70	30.27	20.26	8.77	6.86	10.33	10.41	9.01	9.49	15.00	12.59	8.93	9.73	9.33	8.39
N.A.C. insoluble[a]	3.92	11.19	6.64	19.82	7.00	4.36	2.31	1.64	2.27	1.52	1.16	0.34	0.25	1.12	1.34	0.79	0.77
Water soluble	4.10	1.66	1.66	4.60	6.77	1.37	1.59	5.94	5.39	2.85	3.19	6.28	7.11	2.65	2.64	6.17	5.85
A.C. soluble[b]	5.48	2.65	3.02	2.83	7.23	2.65	3.04	6.41	4.50	6.07	6.99	9.15	9.58	6.42	6.90	5.99	4.17
Fluids analysis, %																	
P_2O_5																	
Product acid	8.10	3.44	3.49	10.7	12.0	3.70	3.80	13.4	13.9	3.45	3.44	12.1	12.4	3.52	3.52	13.3	13.5
First wash	7.97	3.60	3.60	9.92	12.12	3.78	3.93	13.82	14.13	2.94	3.04	12.25	12.64	2.67	2.70	13.62	12.73
Second wash	3.05	1.03	1.69	2.07	5.24	1.43	1.71	5.37	6.97	0.06	0.09	4.59	6.02	0.07	0.07	5.51	6.91
CaO																	
Product acid	0.105	0.09	0.10	0.08	0.08	0.12	0.12	0.10	0.11	0.12	0.12	0.10	0.09	0.12	0.13	0.10	0.10
First wash	0.123	0.12	0.12	0.08	0.08	0.15	0.15	0.11	0.12	0.14	0.15	0.12	0.09	0.15	0.14	0.12	0.12
Second wash	0.115	0.12	0.11	0.09	0.10	0.14	0.13	0.13	0.13	0.10	0.10	0.13	0.10	0.09	0.09	0.15	0.13
Other rock components solubilized, %																	
MgO	101.26	94.5	93.2	91.8	95.9	87.7	127.4	100.0	97.3	110.5	110.5	99.2	96.8	108.1	108.1	100.0	99.2
Fe_2O_3	47.37	30.2	29.8	40.0	45.7	42.0	40.7	66.7	74.8	37.3	37.3	41.7	43.7	43.9	43.9	65.3	74.9
Al_2O_3	59.37	41.8	46.8	63.2	62.7	72.0	80.1	82.2	81.5	38.2	47.6	53.2	14.8	56.0	65.2	69.4	75.2

[a] N.A.C. = neutral ammonium citrate insoluble (A.O.A.C. method).
[b] A.C. = alkaline citrate soluble (exclusive of water soluble).

TABLE 12. EXTRACTION OF PHOSPHATE ROCK WITH WEAK SULFURIC ACID--STATISTICAL EVALUATION OF RESPONSES

Response measured	Overall average	Difference[a] in responses due to variable indicated[b]										Least significant differences		
		A	B	C	D	AB	AC	AD	BC	BD	CD	90	95	99
Filtration rates														
Product acid														
Kg rock/(hr)(m²)	1114	266.5	886.2	613.7	-4.4	-76.7	98.1	107.4	515.1	-59.6	63.0	377.9	481.9	755.8
M³ acid/(hr)(m²)	3.7	1.36	1.66	-4.69	-0.46	-0.99	-1.01	0.11	-0.81	-0.40	0.22	1.21	1.55	2.43
Kg rock P_2O_5/(hr)(m²)	352	60.1	281.7	193.3	-2.9	-34.2	24.4	34.2	160.1	-21.0	18.5	116.7	148.9	233.4
Total filtrate														
Kg rock/(hr)(m²)	357	119.6	138.2	-205.5	-55.2	-72.3	-30.3	4.9	-0.5	-40.0	10.7	125.0	159.2	250.0
M³ acid/(hr)(m²)	3.1	1.14	0.99	-4.03	-0.56	-1.00	-0.82	0.03	-0.52	-0.47	0.31	1.19	1.52	2.38
Chemical responses														
Percent of rock constituent remaining in cake														
CaO	93.62	0.20	-3.22	-0.77	-1.11	-0.45	-0.47	-0.77	-3.79	-2.78	-0.90	3.17	4.05	6.35
P_2O_5														
Total	12.50	-4.38	-6.81	4.15	-2.64	4.38	-2.11	2.12	-3.11	2.14	-0.68	1.85	2.37	3.71
N.A.C. insoluble[a]	3.92	-5.99	-4.17	0.41	-2.38	4.35	-1.15	2.32	-1.32	2.08	-0.70	2.92	3.73	5.85
Water soluble	4.10	0.97	-0.31	3.81	0.34	0.21	-0.29	-0.13	-0.04	-0.50	0.20	0.53	0.67	1.06
A.C. soluble[b]	5.48	2.87	-0.93	1.51	0.41	-1.15	-0.89	-0.41	-1.00	-1.12	-0.13	1.65	2.10	3.29
Fluids analysis, %														
P_2O_5														
Product acid	8.10	0.10	0.95	9.12	0.31	-0.34	0.23	-0.18	0.77	-0.11	0.27	0.29	0.37	0.59
First wash	7.97	-0.29	0.91	9.37	0.29	-0.70	0.60	-0.38	0.93	-0.38	0.22	0.63	0.81	1.26
Second wash	3.05	-0.27	0.91	4.57	1.07	-0.46	1.12	-0.34	0.80	-0.25	0.83	0.44	0.56	0.88
CaO														
Product acid	0.105	0.010	0.015	-0.020	0.003	-0.010	-0.005	-0.003	0.000	0.003	-0.003	0.004	0.006	0.009
First wash	0.123	0.013	0.020	-0.035	-0.003	-0.013	0.003	-0.005	0.005	0.003	-0.003	0.010	0.012	0.019
Second wash	0.115	-0.008	0.018	0.010	-0.008	-0.010	0.022	-0.005	0.012	0.000	-0.002	0.011	0.013	0.021
Other rock components solubilized, %														
MgO	101.26	5.57	4.23	-7.47	4.57	-4.83	-3.03	-5.37	-1.23	4.47	-5.03	9.72	12.40	19.45
Fe_2O_3	47.37	2.26	18.31	18.46	2.96	-1.31	-2.66	-0.06	9.34	1.14	3.39	1.82	2.33	3.65
Al_2O_3	59.37	-13.84	26.66	6.81	-0.26	1.34	-5.41	-3.24	1.94	5.86	-8.19	12.07	15.41	24.16

[a] Negative sign indicates increase in response at the higher level of the variable; underlined values are significant at 90% confidence level.

[b] A = rock particle size, coarse versus fine; B = reaction temperature, 24°C versus 52°C; C = sulfuric acid concentration, 10% versus 30%; D = acid addition time, 1 hour versus 2 hours.

[c] N.A.C. = neutral ammonium citrate insoluble (A.O.A.C. method).

[d] A.C. = alkaline citrate soluble (exclusive of water soluble).

significant differences in averages were derived (90, 95, and 99% confidence levels) and the responses then were evaluated on the basis of these least significant differences.

There are several two-variable interactions that are significant (90% or greater confidence level) and these values are duly listed and underlined in Table 12. However, they will be eliminated from the discussion for the sake of brevity. Only responses to the four individual variables will be discussed.

Filtration Rates--

Filtration rates were calculated as units per hour per square meter of filter area. The units were kilograms of rock, kilograms of rock P_2O_5, and cubic meters of acid. Filtration rates expressed as weight of rock and weight of rock P_2O_5 per hour per square meter responded to temperature and to acid concentration; both higher temperature and stronger acid resulted in higher rates. Neither of the other variables, rock grind or acidulation time, caused significant differences. The slight difference in P_2O_5 content of the two rocks did not cause a significant change in results. When the filtration rates were expressed as volume of acid obtained, response was significant with all variables except acidulation time. Tests with finely ground rock and those made at the higher temperature filtered more rapidly. Tests made with stronger acid filtered more slowly.

Since filtration rates expressed as kilograms of rock and kilograms of rock P_2O_5 gave identical significance of responses, of these two, only the results of calculations showing kilograms of rock per hour per square meter are given. Values for volume of acid obtained are given also. Filtration rate based on weight of rock was significantly responsive only to temperature and acid concentration. Higher temperature increased filtration rates and higher acid concentration decreased rates. Filtration rate based on volume of acid was responsive only to acid concentration. Higher acid concentration decreased rates.

Chemical Responses, Solids--

The solids, after washing and drying as described above, were analyzed chemically, and calculations were made of the proportions of the rock components CaO and P_2O_5 in the solids. Proportions of rock P_2O_5 in neutral ammonium citrate-insoluble, water-soluble, and alkaline citrate-soluble forms were determined. Statistical analyses showed that the proportion of CaO in the solids responded significantly only to variations in temperature; higher temperature resulted in lower recovery of CaO in the solids.

Total P_2O_5 proportion in the solids (cake) responded significantly to all the variables; lower P_2O_5 proportion resulted from the use of the more finely divided rock and from higher temperatures and longer acid addition times. The use of stronger acid increased the proportion of P_2O_5 in the cake. Total P_2O_5 averaged about 12.5% of that present in the rock. The P_2O_5 in the cake was made up of several forms of P_2O_5, and differentiation between these forms is essential to understanding the process. Such differentiation is discussed below.

The proportion of P_2O_5 not extracted by the sulfuric acid may be assumed to be that which appears in the cake as neutral ammonium citrate-insoluble P_2O_5; an average of about 4% of the rock P_2O_5 was insoluble in neutral ammonium citrate. Only two of the variables caused significant responses; the more finely divided rock and the higher temperature resulted in lower citrate-insoluble P_2O_5 content. Neutral ammonium citrate-insoluble P_2O_5 contents as low as 0.8% of the rock P_2O_5 were obtained in tests at the higher temperature with the finer rock.

The proportion of the P_2O_5 in the solids in water-soluble form indicates the effectiveness of the washing procedure. An average of about 4% of the rock P_2O_5 was left in the solids in soluble form; this indicates the need for better washing. The use of the coarser rock and of the lower acid concentration decreased the proportion of water-soluble P_2O_5 in the solids. When using these conditions, as little as 1.7% of the rock P_2O_5 was left in the cake in water-soluble form. Both the more finely divided solids and the increased acid concentration made washing a more significant problem.

The proportion of P_2O_5 in alkaline citrate-soluble form (exclusive of water-soluble portion) represents, to a fair degree of accuracy, that portion present as dicalcium phosphate. Presumably, this represents P_2O_5 that was extracted by the sulfuric acid but was reprecipitated in a water-insoluble form not recoverable from the cake by water washing. This proportion averaged about 5.5% of the P_2O_5 in the rock and varied significantly only with variations in the fineness of the rock; the use of the more finely divided rock resulted in the formation of greater proportions of alkaline citrate-soluble P_2O_5. No reason for this response is immediately evident.

The proportion of P_2O_5 soluble in neutral ammonium citrate solution but insoluble in alkaline citrate solution or in water should represent the reprecipitated P_2O_5 more basic than dicalcium phosphate. This value may be obtained by subtracting the neutral ammonium citrate-insoluble P_2O_5, the alkaline citrate-soluble P_2O_5, and the water-soluble P_2O_5 from the total P_2O_5. The error of all the P_2O_5 analyses contributes to the variation in this value. In the case of the current test series, 12 of the 16 values, so calculated, gave negative results ranging up to 0.88%. Because of this indicated inaccuracy of the data, no statistical analysis of these results was made.

Chemical Responses, Liquids--

True countercurrent washing was not used in these tests; the use of weak phosphoric acid as the first wash solution would have complicated calculations and would have extended the number of tests required. As described earlier, the test procedure included a product acid filtration step in which liquid was collected over the period prior to appearance of solid cake at the slurry surface. At this point, filtration was stopped, the filtrate was isolated, and the first portion of wash water was added to the surface of the cake. Filtration then was resumed until solid cake again appeared at the surface at which time filtration was stopped again and the liquid collected during the first wash period was isolated. The second portion of wash water then was added to the cake surface and filtration was resumed; the time of the first appearance of solid cake was noted but the application of vacuum was continued until "weeping" of the cake had ceased. The liquid from this step then was isolated.

All three liquid samples were submitted for chemical analyses to determine their CaO and P_2O_5 contents. In addition, the MgO, Fe_2O_3, Al_2O_3, F, and SO_3 contents of the first filtrate were determined, also.

The P_2O_5 content of the liquid samples varied within and between the process steps represented. The P_2O_5 contents of all three filtrates varied with the strength of the sulfuric acid used to acidulate the rock; higher sulfuric acid concentrations resulted in higher P_2O_5 contents as expected. Higher P_2O_5 contents in all three filtrates resulted from the use of the higher extraction temperature, also. Higher P_2O_5 contents in the product acid and in the second wash filtrate were obtained as a result of the longer retention time; it is not obvious why this variable did not affect the P_2O_5 content of the first wash filtrate as significantly. The average P_2O_5 content of the product acids was 12.66% for the 30% sulfuric acid tests and 3.54% for the 10% sulfuric acid tests. The average P_2O_5 content for the first wash filtrates was 12.65% (30% H_2SO_4) and 3.28% (10% H_2SO_4). Second wash filtrate P_2O_5 analyses averaged 5.34% (30% H_2SO_4) and 0.77% (10% H_2SO_4).

The CaO analyses of all the liquid samples were very near the same value. All values were within the range 0.115 ± 0.035%. Consequently, a high degree of significance was attributed to variations in average analyses as low as 0.0045%, a value smaller than the precision of the analyses. The indicated responses, therefore, may not be as significant as indicated. Greatest variations were caused by variations in sulfuric acid concentration and test temperature. Proportion of CaO was greatest at the lower acid concentration and highest temperature. The proportion of the rock CaO dissolved in these tests is much greater than would be expected from processes producing stronger acids. A correlation of CaO content and acid concentration will be given later.

Evaluation of the proportions of MgO, Fe_2O_3, and Al_2O_3 extracted were based on comparisons of the ratio of those components to P_2O_5 content in the rocks with the ratio of those components to P_2O_5 derived from the rocks in the strong acid filtrates. Essentially all the MgO was extracted; the average value for all the tests was 101.26%, the range was 90 to 130%. Analytical values were so small that precision was a major problem. None of the variables affected the proportion of MgO extracted at the 90% confidence level.

An average of about 47% of the Fe_2O_3 in the rocks was extracted. The proportion of Fe_2O_3 extracted was responsive to changes in temperature, sulfuric acid concentration, and time used in the tests. Increasing each increased Fe_2O_3 extraction. Response to rock grind, although significant statistically, was based on variations in analyses less than the precision of the analyses.

An average of about 60% of the Al_2O_3 in the rocks was extracted. The proportion of Al_2O_3 was varied by changes in rock grind and temperature. Fine grinding of rock resulted in reduced extraction. This does not appear reasonable and may indicate an erroneous rock analysis although the reported Al_2O_3 content of the rock (1.1%) appears reasonable. The most effective of the variables was temperature; higher temperatures resulted in greater Al_2O_3 extraction.

In addition to the tests performed as a part of this factorial experiment, individual tests were made using 5, 15, and 60% H_2SO_4 at the same conditions as the tests reported in positions 14 (10%) and 16 (30%). From the results of these tests, a chart was prepared (Figure 25) to show the effects of acid concentration on extraction of the various components of the rock. The values plotted are the weight ratio of the extracted metal oxide to extracted P_2O_5 versus the H_2SO_4 concentration used to extract the rock. The plot shows little effect on the proportions of MgO or Al_2O_3 extracted. Extraction of Fe_2O_3 was minimized by reducing H_2SO_4 concentration; this same condition maximized CaO solubilization.

Conclusions

It is concluded that beneficiated phosphate rock may be extracted to a reasonably high degree (above 99% of P_2O_5 in citrate-soluble form) with sulfuric acid of low (5-30%) concentration and that extraction is improved with increases in temperature and fineness of rock grind. Increasing acidulation time from 1 to 2 hours did not improve P_2O_5 extraction or filtration rates significantly. Overall filtration rates, expressed as kilograms of rock per hour per square meter, were improved by increasing the temperature and by decreasing acid concentration. The average filtration rate was 357 kilograms of rock per hour per square meter of filter surface; the range was 154 to 595 kilograms of rock per hour per square meter. Extraction of Fe_2O_3 was minimized without increase in extraction of MgO or Al_2O_3 by use of weaker sulfuric acids. However, the solubility of CaO in the acid increased as the acid concentration was decreased, and any subsequent thermal concentration probably would result in troublesome precipitation of calcium sulfate. The increased solubility of CaO emphasizes the need for methods of concentration not dependent on evaporation of water.

PRODUCTION OF WET-PROCESS ACID FROM UNBENEFICIATED MATRIX

During the beneficiation of phosphate rock matrix to a salable grade of raw material for the production of wet-process phosphoric acid, as much as 40% of the phosphate in the matrix may be lost to slime waste. This loss of valuable material and the associated problems of slime disposal are areas of increased concern for the phosphate industry. The use of unbeneficiated phosphate rock matrix for the production of wet-process acid should reduce the loss of phosphate and eliminate the necessity for slime disposal ponds. Weak sulfuric acid ($< 30\%$ H_2SO_4) might be available from some pollution control processes, including those utilizing carbon adsorption-water elutriation.

Test Plan and Equipment

A factorially designed experiment has been made in which two different samples of Florida phosphate matrix were extracted with dilute sulfuric acid to produce phosphoric acid by the wet process. Acid proportion used was 1 mole H_2SO_4 per mole of CaO in the matrix. The experiment was made to determine the effects of different matrix samples, matrix treatment, acid concentration, and temperature on the extraction of various matrix components. The test parameters are shown below; the full test plan is shown in Table 13.

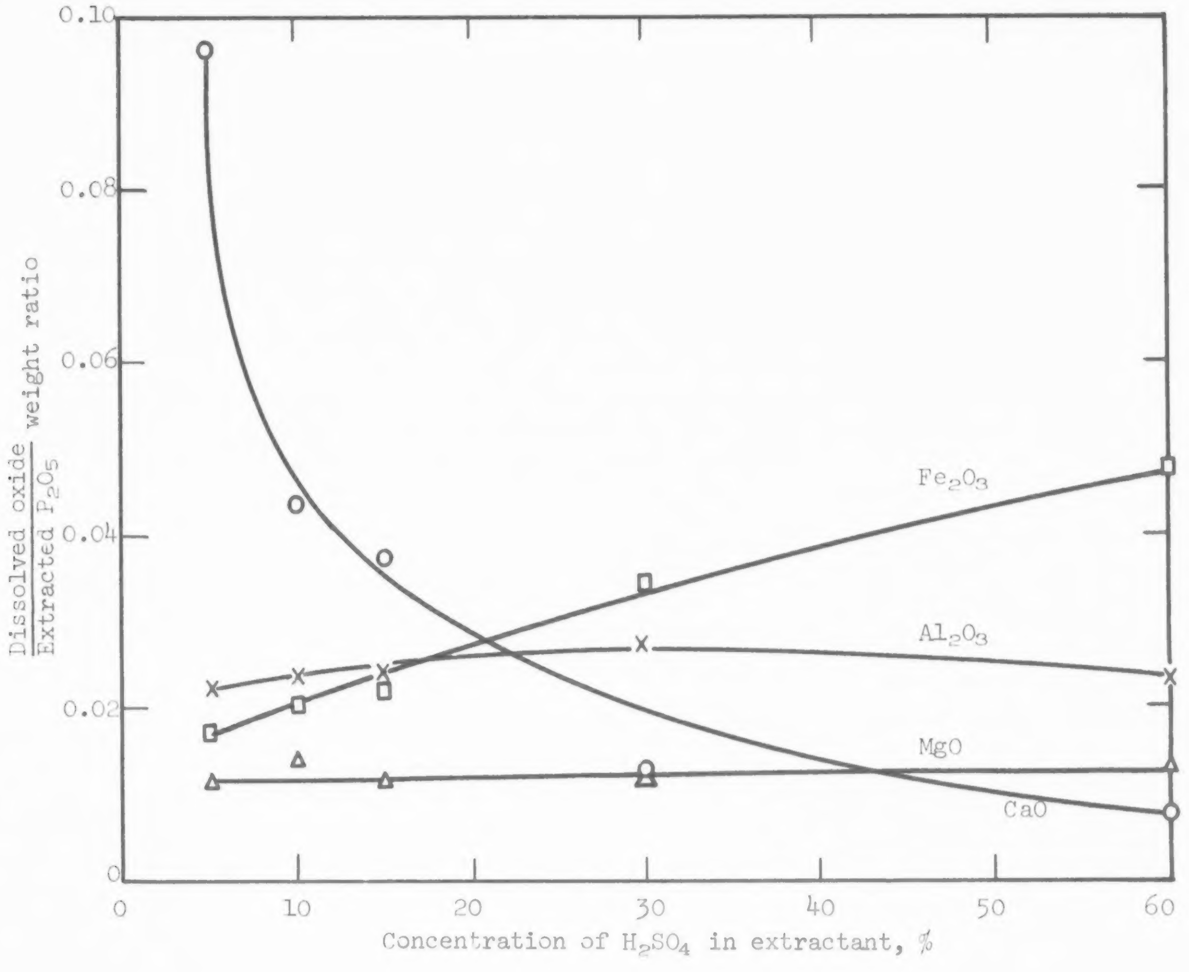


Figure 25. Effect of concentration of H_2SO_4 on dissolution of metal oxides from phosphate rock.

TABLE 13. UTILIZATION OF LOW-GRADE PHOSPHATES--TEST PLAN

Test position	Test No.	Variables			
		Matrix source[a]	Matrix treatment[b]	H_2SO_4 concentration, %[c]	Temperature, °C
1	1	FM30	Raw	10	Ambient
2	3	FM30	Raw	10	52
3	4	FM30	Raw	25	Ambient
4	6	FM30	Raw	25	52
5	7	FM30	Calcined	10	Ambient
6	5	FM30	Calcined	10	52
7	2	FM30	Calcined	25	Ambient
8	8	FM30	Calcined	25	52
9	1B	FM20	Raw	10	Ambient
10	3A	FM20	Raw	10	52
11	4B	FM20	Raw	25	Ambient
12	6A	FM20	Raw	25	52
13	7A	FM20	Calcined	10	Ambient
14	5A	FM20	Calcined	10	52
15	2B	FM20	Calcined	25	Ambient
16	8A	FM20	Calcined	25	52

[a] Phosphate matrix samples from two Florida fields:

	Chemical analysis, %					
	P_2O_5	CaO	Fe_2O_3	Al_2O_3	MgO	F
FM30--raw	11.8	18.0	1.48	2.6	0.44	1.4
FM30--calcined	13.0	19.7	1.64	2.9	0.48	1.3
FM20--raw	18.1	27.4	1.56	2.2	0.67	2.1
FM20--calcined	13.6	28.3	1.64	2.4	0.68	2.0

[b] Raw matrix--Florida phosphate matrix as received.
Calcined matrix--raw matrix calcined at 982°C for 90 minutes.

[c] Actual concentration used: FM30 matrix, 9.34 and 25.15% H_2SO_4; FM20 matrix, 9.77 and 28.34% H_2SO_4.

	Level	
	-	+
Matrix source[a]	FM30	FM20
Matrix treatment	Raw	Calcined[b]
H_2SO_4 concentration, %	10	25
Temperature, °C	Ambient	52

a. Chemical analyses of matrices given in Table 13.

b. Calcined at 982°C for 90 minutes.

The equipment used was the same as that used in previous extraction tests with weak acid described earlier. Also, the test procedure was the same, with the following exceptions. The agitator speed was increased to 500 rpm for all tests and the volume of the prewet acid was increased to 260 milliliters for the tests in which 25% sulfuric acid was used. These changes were required because of the consistency of the reaction mixture during the acidulation period resulting from the larger amount of clay in the matrix as compared with beneficiated rock. Also, because of the long filtration times encountered in preliminary tests (as long as 1 hr for acid separation and as long as 4 hr for wash separation), each acidulated mixture was poured into a 1-liter graduated cylinder immediately after the final 15-minute agitation period and allowed to settle until separated. After the volume of the solid layer became essentially constant, the clear liquor was siphoned off. The solid layer then was elutriated with water twice, each time filling the graduate to a total volume of 1 liter and allowing the solids to settle to approximately the same volume as in the initial separation. The solids were then transferred to the 100-mesh screen filter and allowed to pull dry under a 38 centimeter mercury (15 in Hg) vacuum before being oven dried at 52°C. The weighed and dried filter cakes were submitted for chemical analysis. The observed test data, the analyses of the dried cakes, and the calculated proportions of the matrix components extracted or left in the cakes (chemical responses) are given in Table 14. A large proportion of the product acid was derived from recycled reagent-grade acid rather than from the matrix; for this reason, the evaluation was made from cake analyses.

Evaluation of Data

Evaluation of the test results was made using the statistical analysis of the responses. The values given in Table 15 are the overall averages of the responses for each variable and the differences in responses due to changing the level of the indicated independent variable. Originally, it was assumed that the three- and four-factor interactions would be highly unlikely and therefore could be combined to form an estimate of the error; however, it was found that the three-factor interaction of matrix source, matrix treatment, and acid concentration (ABC interaction) was significant. Thus, that interaction was not combined with the error in the final analysis.

TABLE 14. UTILIZATION OF LOW-GRADE PHOSPHATES--TEST RESULTS

	Test position															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Primary data																
Separation to recover H_3PO_4																
Time allowed to settle, hr	23.5	118	114	90	27	94	44	51	69	46	55	76	28	25	50	44
Volume clear liquor, ml	214	240	165	145	480	105	87	375	355	290	10	80	120	230	40	45
Volume solid layer, ml	238	180	210	205	385	275	320	275	235	290	435	330	500	385	400	360
Weight dry cake, g	106.0	103.7	103.1	102.4	114.4	109.9	113.4	112.1	117.0	118.7	112.8	109.2	128.7	124.6	116.9	120.8
Chemical analysis of dry cake, %																
CaO	13.2	14.5	13.0	12.0	14.6	15.7	14.4	14.8	20.9	20.2	21.1	21.5	21.0	21.7	19.7	18.9
MgO	0.13	0.05	0.03	0.02	0.08	0.07	0.08	0.05	0.05	0.04	0.02	0.03	0.22	0.23	0.03	0.10
Fe_2O_3	0.95	0.08	0.41	0.52	0.69	0.54	0.65	0.57	0.57	0.67	0.13	0.15	0.59	0.69	0.16	0.37
Al_2O_3	0.83	0.42	0.27	0.18	0.26	0.17	0.41	0.20	0.40	0.32	0.17	0.20	0.39	0.36	0.20	0.22
SO_3	17.0	19.7	18.1	16.8	20.0	21.6	19.8	20.2	28.0	27.9	30.1	29.7	28.5	28.6	26.5	25.9
P_2O_5																
Total	1.3	0.9	0.9	0.7	1.1	0.7	1.5	1.1	1.6	1.3	2.1	2.7	2.7	1.6	2.4	2.2
N.A.C. insoluble[a]	0.3	< 0.1	< 0.1	< 0.1	0.2	0.2	< 0.1	< 0.1	0.3	0.05	0	0	0.3	0.8	0	0.05
Water soluble	0.4	0.4	0.5	0.4	0.5	0.3	0.7	0.7	0.8	0.7	1.8	2.3	1.8	0.5	2.1	1.9
Chemical responses																
Cake components, % of that present in matrix																
CaO	77.7	83.5	74.5	68.3	84.6	87.6	82.9	84.2	89.4	87.7	87.0	85.8	95.5	95.5	81.4	80.7
MgO	31.3	11.9	7.0	4.7	19.2	16.2	19.1	11.8	8.7	7.1	3.4	4.9	41.6	42.1	5.2	17.8
Fe_2O_3	68.0	56.1	28.6	36.0	48.1	36.2	45.0	39.0	41.7	49.7	9.2	10.2	47.5	53.7	11.7	27.9
Al_2O_3	33.8	16.8	10.7	7.1	10.2	6.4	16.0	7.7	21.3	17.3	8.7	9.9	20.9	18.7	9.7	11.1
P_2O_5																
Total	11.7	7.9	7.9	6.1	9.7	5.9	13.1	9.5	10.3	8.5	13.1	16.3	18.7	10.7	15.1	14.3
N.A.C. insoluble[a]	2.7	0.4	0.4	0.4	1.8	1.7	0.4	0.4	1.9	0.3	0	0	2.1	5.4	0	0.3
Water soluble	3.6	3.5	4.4	3.5	4.4	2.5	6.1	6.0	5.2	4.6	11.2	13.9	12.4	3.3	13.2	12.3
Reprecipitated[b]	5.4	4.0	3.1	2.2	3.5	1.7	6.6	3.1	3.2	3.6	1.9	2.4	4.2	2.0	1.9	1.7
P_2O_5 extracted,[c] % of input matrix P_2O_5	97.3	99.6	99.6	99.6	98.2	98.3	99.6	99.6	98.1	99.7	100	100	97.9	94.6	100	99.7

[a] N.A.C. insoluble = neutral ammonium citrate insoluble (AOAC method).

[b] Reprecipitated apatite P_2O_5, calculated as (total P_2O_5) - (water-soluble P_2O_5) - (N.A.C. insoluble P_2O_5).

[c] Extracted P_2O_5 calculated as 100 - (N.A.C. insoluble P_2O_5).

TABLE 15. UTILIZATION OF LOW-GRADE PHOSPHATES--EFFECTS OF VARIABLES

		Difference[a] in average of responses due to variable[b] indicated										
	Overall average	Matrix source (A)	Matrix treatment (B)	H_2SO_4 conc'n (C)	Temperature (D)	(AB)	(AC)	(AD)	(BC)	(BD)	(CD)	(ABC)
Chemical responses												
Matrix components in cake, % of input												
CaO	84.1	7.46	4.81	-7.09	0.04	-4.01	-1.21	-0.94	-1.41	0.86	-1.74	-4.74
P_2O_5												
Total	11.2	4.40	1.90	1.50	-2.55	0.75	1.15	0.70	0.25	-1.50	1.80	-2.90
N.A.C. insoluble[c]	1.1	0.23	0.75	-1.80	-0.05	0.65	-0.55	0.55	-0.68	0.93	0.13	-0.58
Water soluble	6.9	5.26	1.29	3.89	-1.36	0.29	2.39	-0.61	-0.14	-1.64	1.56	-1.24
Reprecipitated[d]	3.2	-1.09	-0.14	-0.59	-1.14	-0.19	-0.69	0.76	1.06	-0.79	0.11	-1.09
Matrix components solubilized,[e] % of input												
MgO	84.3	-1.20	-11.75	13.03	2.38	-8.90	4.03	-5.63	3.28	-3.08	-3.50	10.03
Fe_2O_3	62.0	13.18	-1.20	24.18	-1.13	-6.30	9.23	-6.73	-8.70	0.00	-3.53	6.10
Al_2O_3	85.9	-1.11	3.11	8.06	4.54	-3.91	1.64	-3.64	-5.14	-1.31	-2.21	4.84
P_2O_5 extracted, % of input matrix P_2O_5	98.9	-0.23	-0.75	1.8	0.05	-0.65	0.55	-0.55	0.68	-0.93	-0.13	0.58

[a] Negative sign indicates a decrease in response at the higher level of the variable; underlined values are significant at 90% confidence level.

[b] A = rock source FM30(-) vs. FM20(+) B = matrix treatment raw(-) vs. calcined(+) C = H_2SO_4 concentration 10%(-) vs. 25%(+) D = reaction temperature ambient(-) vs. 52°C (+)

[c] N.A.C. insoluble = neutral ammonium citrate insoluble (AOAC method).

[d] Reprecipitated apatite P_2O_5 calculated as (total P_2O_5) - (water-soluble P_2O_5) - (N.A.C. insoluble P_2O_5).

[e] Calculated from cake analyses.

Thus, using this esimate of error, the responses for three of the dependent variables were rejected because of a lack of significant difference between the error and the model. Those dependent variables are the neutral ammonium citrate-insoluble P_2O_5 and the water-soluble P_2O_5 in the cake and the P_2O_5 extracted from the matrix. The models for all other dependent variables were found to be significantly different from the error, and therefore their responses which produced significant differences (at least 90% confidence) between the levels of each of the independent variables and their interactions are duly underlined in Table 15.

There are several two-factor and one three-factor interactions which are significant and those results are listed in Table 15. However, in the interest of brevity they will be omitted from the discussion. Only the results of the four individual independent variables will be discussed.

Chemical Responses, Solids--

The proportion of CaO left in the cake (an average of 84.1% of input) was affected by three of the independent variables. More CaO was left in the cake (a desirable condition) when the matrix FM20 was used and when the matrix was calcined before extraction. Less CaO was left in the cake when the more concentrated acid was used.

The quantity of total P_2O_5 remaining in the cake averaged 11.2% of input. Its removal was enhanced with the use of matrix FM30, with the use of uncalcined matrix, and with the higher level of temperature. The greatest of these effects was due to the matrix source. It is noted, however, that the total P_2O_5 content of the cake includes all forms of P_2O_5 and therefore is subject to variations in extraction, washing, and reprecipitation. In the tests conducted (Table 14) lowest retention in the cake was 5.9% in test position 6 (-A, +B, -C, +D).

As previously stated, the responses for neutral ammonium citrate-insoluble, water-soluble, and the extracted (citrate-soluble) forms of P_2O_5 were rejected because of their lack of significance. The acidulation procedure extracted the P_2O_5 so completely (average 98.9%) that the differences between the tests were insignificant. In the separation of the solids, however, the removal of solubilized P_2O_5 from the cake varied widely; solubilized P_2O_5[1] not removed averaged about 10% of the matrix P_2O_5. The values were so distributed, however, that the model did not define the causes adequately. However, values for the reprecipitated P_2O_5 (citrate-soluble but water-insoluble P_2O_5) did show a high probability of being significant (94.8% confidence in the model). If this degree of confidence is accepted, the amount of P_2O_5 precipitated was minimized both with the use of matrix FM20 and with the higher temperature. In the tests made (Table 14), the average amount reprecipitated was 3.2% of the P_2O_5 in the matrix; minimum precipitation (1.7%) was in test positions 6 and 16 (-A, +B, -C, +D and +A, +B, +C, +D).

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[1] Solubilized P_2O_5 not removed = (total P_2O_5) - (N.A.C. insoluble P_2O_5).

Further evaluation, based on solids analysis, was made to determine the proportions of the other rock components solubilized. The solubilization of MgO, a contaminant in product acids, averaged 84% of input for all the tests. Its solubilization was reduced with the use of the weaker acid and also with calcination of the matrix. In the tests made (Table 14), minimum solubilization (57.9%) was in test position 14 (+A, +B, -C, +D). The other variables did not produce changes significant at the 90% confidence level; the three significant two- and three-factor interactions are noted.

The solubilization of Fe_2O_3, another contaminant in product acid, averaged 62% of input for all the tests. The use of matrix FM30 reduced the solubilization of this species. A greater effect was caused by the sulfuric acid concentration. An average of 50% of the input Fe_2O_3 was solubilized when the more dilute (10%) acid was used while 74% was found in the product made with the more concentrated (25%) sulfuric acid.

A third common contaminant of wet-process acid, Al_2O_3, was removed from the matrix at an average of 86% of input for all the tests. Its solubilization was decreased by using the weaker acid and by the use of the lower (ambient) temperature with the greater effect due to acid concentration. In the tests made (Table 14), the minimum solubilization (66%) was in test position 1 (-A, -B, -C, -D).

In the production of wet-process phosphoric acid, the product acid concentration depends on the amount of P_2O_5 extracted and on the water balance in the system. If good extraction is attained and if washing is good (nearly all interstitial liquor in the cake is water and little or no wash water in the recycle acid), the product acid concentration will be dependent on the concentration of the sulfuric acid, the amount of water evaporated, and the amount of water removed by hydration of the calcium sulfate.

For these tests, a product acid concentration was calculated assuming complete extraction and perfect washing. As mentioned earlier, when 10% H_2SO_4 was used, the phosphoric acid concentration was calculated to be about 5.7% or 4.1% P_2O_5; with 25% H_2SO_4, the values would be 21.4 and 15.5%, respectively. In tests made with 10% H_2SO_4, the actual product acid averaged 6.39% H_3PO_4 and with 25% H_2SO_4, 23.87% H_3PO_4. A large portion of these products, however, was derived from the starting recycle acids.

The product acids would contain an average of about 16% of the CaO, 62% of the Fe_2O_3, 86% of the Al_2O_3, and 84% of the MgO originally present in the rock. These values are based on the observed proportions of these components in the filter cake. An acid produced from a blend of the matrix samples and the average sulfuric acid concentration used in the current tests would have the following analysis: P_2O_5, 9.8%; CaO, 2.3%; Fe_2O_3, 0.62%; Al_2O_3, 1.38%; and MgO, 0.3%. The ratios of impurities to P_2O_5 are greater than in commercial acid because of the greater solubility in the weak acid, because of the higher ratios in the matrix, or both.

These current tests may be compared with the previously reported tests which were also made in a factorially designed experiment but which utilized a normal grade rock. Two of the independent variables studied, temperature and acid concentration, were the same in both series of tests (rock grind and acid addition time were the other variables in the earlier tests). Previously, it was found that temperature produced significant responses in more of the dependent variables than acid concentration; in the present tests the opposite was true. However, where significant responses coincide for both experiments, the directions of the responses were the same. In both experiments, decreasing the sulfuric acid concentration decreased the solubilization of Fe_2O_3. Likewise, decreasing the reaction temperature decreased the solubilization of Al_2O_3 and the recovery of total P_2O_5.

Conclusions

The results of this study indicate that a large increase in the recovery of P_2O_5 from phosphate rock would result from the acidulation of the raw matrix rather than flotation concentrate. Large amounts of P_2O_5 may be lost in the flotation process. An average of about 99% of the P_2O_5 in the matrix was solubilized in these tests. There was an increase in sulfuric acid requirement but that acid would be recovered from flue gas desulfurization processes.

Advantages accruing to the use of weak sulfuric acid to acidulate raw matrix include lower solubilization of MgO, Fe_2O_3, and Al_2O_3 from the rock which is highly desirable. Calcination of the rock further reduced MgO solubilization. Maintaining low temperatures during extraction reduced Al_2O_3 solubilization. The proportion of Fe_2O_3 solubilized was a function of the source of the rock also.

Disadvantages are concerned with the poor filtration rates and the need to dispose of large amounts of solids. A settling system ahead of the filter might be required.

It was concluded that the production of phosphoric acid from raw phosphate matrix and weak sulfuric acids at or near the source of the weak acid would be technically feasible.

CONCENTRATION OF PHOSPHORIC ACID BY FREEZING

The use of weak sulfuric acid to extract phosphoric acid from phosphate rock will result in the production of relatively weak phosphoric acid (generally $< 30\%$ H_3PO_4). The weak phosphoric acid would be a more useful product if it were concentrated to filter-grade acid (about 40% H_3PO_4) or, even better, to a shipping-grade level (about 70% H_3PO_4).

Experimental Work

A short literature search indicated that some energy savings over usual heating methods of concentration might result from freezing of water from the acid and mechanically removing the ice from the acid mother liquor. Laboratory investigations have been made of the concentration of industrial wastes (8) by freezing and a process for desalination of seawater (9, 10) by freezing is close to commercialization. Both procedures are reported to function well. Some energy might be saved since freezing water requires removal of 80 calories per gram while evaporation requires the addition of 539 calories per gram.

Published data on the freezing point of aqueous solutions of phosphoric acid are given in Figure 26. A brief investigative program was started to study the problems which might develop from attempts to concentrate acid by freezing. Initial attempts indicated that a primary problem would be the recovery of large amounts of H_3PO_4 left in the ice as interstitial liquor. The removal of this liquor, probably the strongest acid in the system at the time of ice formation, would be necessary. Early tests indicated that the amount of interstitial liquor retained was approximately equal to the amount of ice formed. A practical approach appeared to be to attempt concentration by 1.5 times (from 10-15% H_3PO_4); this should result in approximately one-third each of ice, interstitial liquor, and product acid.

The interstitial liquor problem might be minimized by washing ice on a filter with a minimum amount of water at 0°C to remove acid without excessive dilution of the acid. A few exploratory tests were conducted to check this procedure.

An 8-liter cold bath capable of operation to -50°C was filled with a commercial antifreeze solution of ethylene glycol and water and was set at -4°C. A closed vessel containing about 100 grams of 10% H_3PO_4 (prepared from reagent H_3PO_4) was placed in the cold bath and was cooled to -4°C. No crystallization was apparent until the sample was seeded with a few small crystals of ice; it then was allowed to equilibrate overnight before it was filtered using the laboratory vacuum system. There was 50.5 grams of filtrate obtained indicating that warm air leaking through the vacuum filter probably caused some melting of ice and washing of interstitial acid into the product. Titration with 0.2 N NaOH indicated the product contained about 14.8% H_3PO_4. The remaining ice was melted, weighed, and analyzed. Results indicated that about 44.1 grams was obtained which contained about 5.1% H_3PO_4. A calculated 94.4% of the acid was recovered with 76.9% of the recovered acid being in the filtrate.

A second sample was placed in the bath with a small glass propeller-type stirrer in the sample (stirrer operated at about 100 rpm). The intent was to cool the sample rapidly to about -1°C and then at a rate of about 0.5°C every 5 minutes to -4°C. The intended rate was attained to about -2°C when the sample was seeded (with ice) and equilibration begun. A difference in temperature between the cold bath and sample of only about 0.5°C was sufficient for the initial cooling. Afterward, the time required for the sample to equilibrate and cool an additional 0.5°C was over 30 minutes in spite of an increase in difference between the sample and bath of over 2.75°C. At least an equal period was required before the sample reached -4°C with the temperature differential increased to as much as 8°C at times. The ice clung to the sample container and could not be poured onto the filter. Only 12.3 grams of filtrate was obtained. No analyses were made.

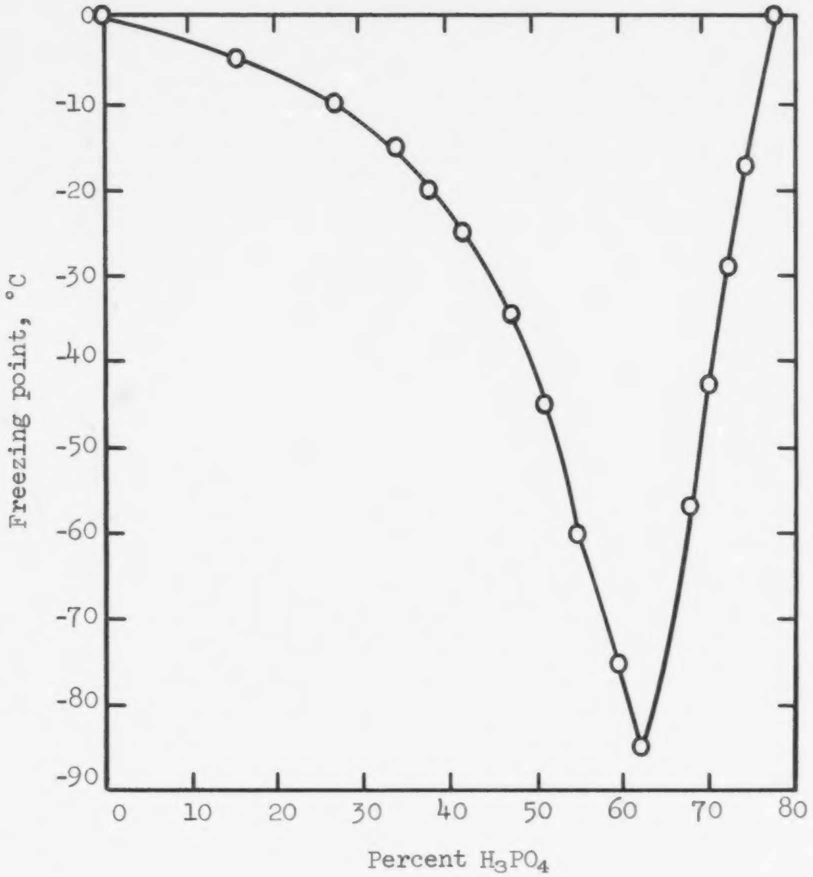


Figure 26. Freezing point of phosphoric acid. (11)

The test was repeated with the exception that the ice was scraped into the filter, the filter was maintained at test temperature by immersion in the cold bath, and a single wash with 30 grams of ice water was used. The glass stirrer was operated at 500 rpm until crystallization started and then the speed was increased to 1000 rpm. The sample was cooled to -1°C rather rapidly. The bath was then lowered to -2.5°C (0.5°C below the expected ice point) in about 5 minutes and was held there until ice remained frozen after seeding; the batch temperature was then kept at -3.3°C until the sample appeared to equilibrate at about -2°C (an additional 20 minutes was required). The bath temperature was then decreased to maintain a maximum differential temperature of less than 2°C in an attempt to increase crystal size. Movement of ice in the sample became extremely slow when the sample reached -2.8°C and cooling was stopped when the sample reached -3°C (essentially no movement of ice). The sample and ice were transferred to a filter and a slight vacuum was applied; filtrate weight was 43.0 grams. A 30-gram ice-water wash was then applied from which apparently some water was frozen since only 16.2 grams of wash solution was recovered. The ice was then allowed to melt and was transferred to a sample bottle; 68.4 grams of solution was obtained. Titrations of the portions indicated the filtrate contained 14.9% H_3PO_4, the wash contained 14.3%, and the ice contained 2.4% H_3PO_4. Thus, 61.8% of the acid was in the filtrate, 22.4% in the wash, and 15.8% in the ice.

The test was repeated using three 30-milliliter portions of ice water as wash. The cooling and stirring rates were approximately the same as in the test above. The results obtained are shown below.

	Filtrate	Wash 1	Wash 2	Wash 3	Ice
Weight, g	41.9	16.4	34.3	27.6	64.7
% H_3PO_4	14.2	12.4	4.2	1.2	0.5
% of recovered H_3PO_4	59.2	20.2	14.2	3.2	3.2
Indicated % of input H_3PO_4	60.6	20.7	14.6	3.2	3.3

Again a portion of the first wash may have been frozen by the ice (recovered only 16.4 g of 30-g wash). It might be possible to wash the ice in a countercurrent procedure and add the first wash filtrate to the product acid. A process can be envisioned which includes a series of such countercurrent washes so that the overall acid recovery might be acceptable. The recovery in each step would diminish rapidly, however, and further washing would soon become uneconomical. In the above example with three water washes, the recovery of acid as product and wash solution was nearly 97%; this recovery might be approached if the washing were done with decreasing strengths of acid rather than with water.

A projected flowsheet for a three-step concentration process is shown in Figure 27. Concentrations of the wash liquors shown in this figure are estimated; actual values depend on the washing efficiency, the amount of ice melted or water frozen, and the concentrations of the incoming streams. The concentration of the liquor in the freezing steps would depend on the temperature attained, the degree of supercooling resulting from the procedure, and the effects of impurities on the freezing point of the mixture. First-stage concentration would be from 10 to 15%, as studied in the earlier tests. Second- and third-stage concentrations would be from 15 to 22% and 22 to 33%,

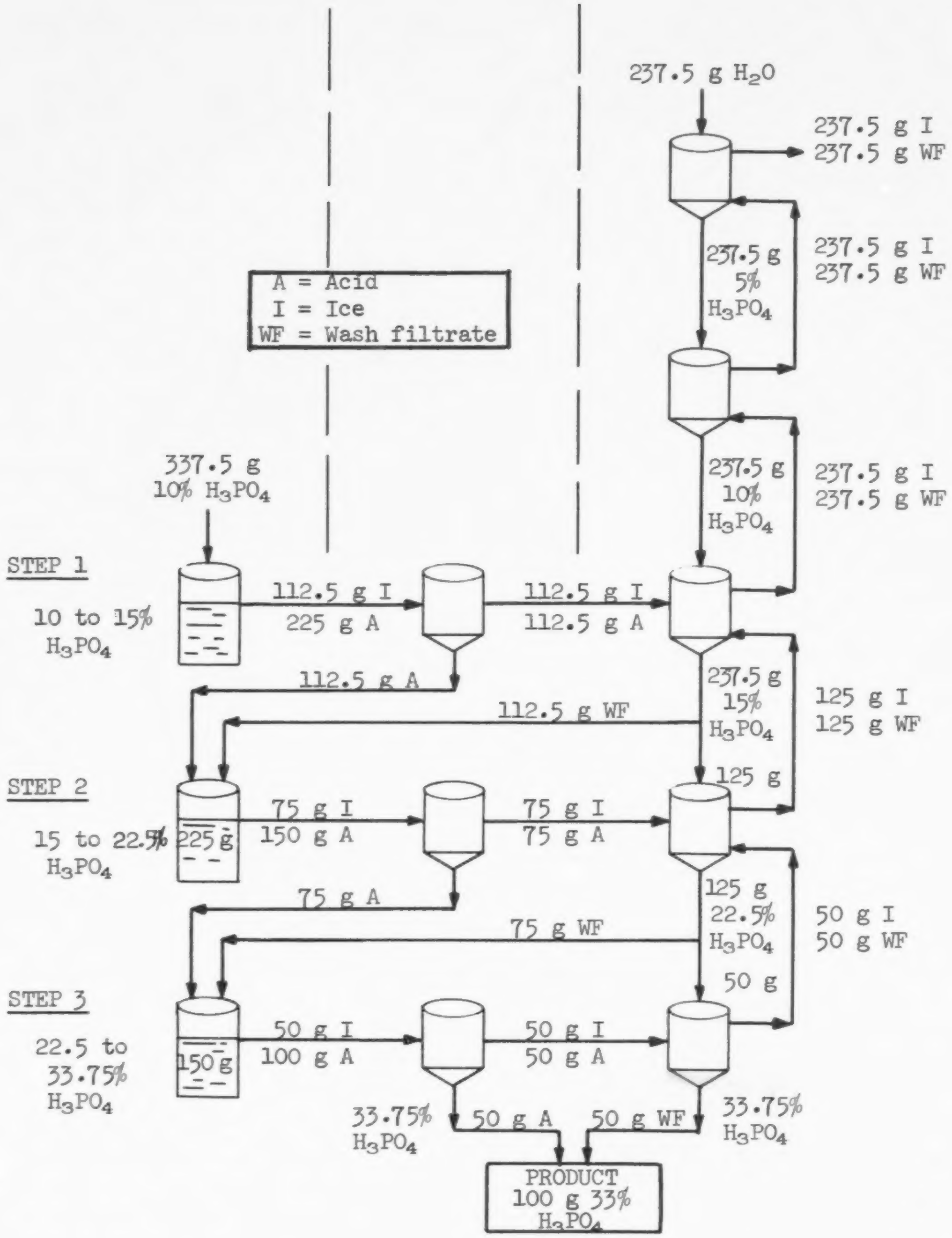

237.5 g H_2O
237.5 g I
237.5 g WF
237.5 g 5% H_3PO_4
237.5 g I
237.5 g WF
A = Acid
I = Ice
WF = Wash filtrate
337.5 g 10% H_3PO_4
237.5 g 10% H_3PO_4
237.5 g I
237.5 g WF
STEP 1
10 to 15% H_3PO_4
112.5 g I
225 g A
112.5 g I
112.5 g A
112.5 g A
112.5 g WF
237.5 g 15% H_3PO_4
125 g I
125 g WF
125 g
STEP 2
15 to 22.5% H_3PO_4
225 g
75 g I
150 g A
75 g I
75 g A
75 g A
75 g WF
125 g 22.5% H_3PO_4
50 g I
50 g WF
50 g
STEP 3
22.5 to 33.75% H_3PO_4
150 g
50 g I
100 g A
50 g I
50 g A
33.75% H_3PO_4
50 g A
50 g WF
33.75% H_3PO_4
PRODUCT
100 g 33% H_3PO_4

Figure 27. Projected flowsheet for concentration of dilute phosphoric acid by three-step batch freezing.

respectively. Concentration higher than 33% would require temperatures lower than are considered practical. One test was made of concentration over each of the three ranges. For each test, fresh acid feed was made to the desired concentration by diluting reagent-grade phosphoric acid. The filter cake washing procedure was varied somewhat from that indicated in Figure 27, as will be discussed.

The procedure in each of the present three tests comprised the following steps. Phosphoric acid at the initial concentration was stirred constantly and cooled rapidly in a bath to a point near its predicted freezing point. The bath then was cooled slowly until the acid reached the predicted freezing point, at which time it was seeded with a small amount of ice. After ice formation was initiated, the agitation rate was increased and the bath was cooled further until the acid-ice mixture reached the predicted freezing point of the desired product acid or until the mixture became too viscous to stir. Care was taken to prevent a large temperature differential between the bath and the acid-ice mixture; a 3°C differential was the maximum allowed. Usually, about 1 hour was utilized in cooling the acid sufficiently to result in a 50% increase in concentration. The acid-ice mixture then was filtered on a medium fritted glass funnel which had been cooled in the same bath in which the ice was formed. The ice cake subsequently was washed with ice water or a series of weak phosphoric acid solutions as described later. After washing, the ice was allowed to melt and the strong filtrate, washes, and melted ice were separately weighed and analyzed titrimetrically to determine the concentration and distribution of the phosphoric acid.

Data from the tests are given in Table 16 and Figure 28. The figure shows the temperature-time relationships of the bath and the acid for the three tests in which the aim was to concentrate acid from 10 to 15%, to 22.5%, and finally to 33.75% H_3PO_4. The freezing points of the acid at each concentration and the point at which seed ice was added are shown also. The table gives the initial concentration (intended) and weights of the acids and the temperatures at which they were seeded and to which they were cooled after seeding. Also listed are the compositions and weights of the wash solutions and of the various products. A percentage distribution of phosphoric acid in the final products is given also.

In test 1, approximately 10% H_3PO_4 was cooled rapidly to -1°C and then cooled slowly to -1.94°C before being seeded with a few crystals of ice scraped from the surface of equipment extending above the liquid level in the cold bath. Ice began to form in the solution and then to grow in quantity until the test was stopped with a sample temperature of -3.06°C and a bath temperature of -4.17°C. At this time, the ice-acid slurry was transferred to the cold filter (immersed in the same cold bath) and filtered under low vacuum (estimated at 71 cm Hg absolute) to recover 43 grams of acid having a concentration of 14.9% H_3PO_4. The remaining ice (67 g, including interstitial liquor) then was washed with 30 grams of water at 0°C on the same filter and 16.2 grams of filtrate was recovered which analyzed 14.3% H_3PO_4. The remainder of the ice-liquor cake was allowed to melt; 68.4 grams of liquor was recovered which contained 2.4% H_3PO_4. In the test, 127.6 of the 130 grams of input weight was accounted for (98.15% of total). The accounted for phosphoric acid was distributed so that 61.8% was in the first filtrate, 22.4% was in the wash,

TABLE 16. LABORATORY-SCALE BATCH TESTS OF CONCENTRATION OF DILUTE PHOSPHORIC ACID SOLUTIONS BY FREEZING

Test No.	1			2				3				
Freezing												
Feed acid												
Conc., % H_3PO_4	9.85			15.23				22.45				
Weight, g	100			100				100				
Temperature, °F												
Precool	20.2			28.8				20.8				
When seeded	28.5			25.3				18				
Final	26.5			19.0				15.0				
Filtration												
Step	Filtrate	Wash	"Ice"	Filtrate	Wash	Wash	"Ice"	Filtrate	Wash	Wash	Wash	"Ice"
Wash												
Conc., % H_3PO_4	-	0.0	-	-	15.23	9.85	-	-	22.45	22.45	15.23	-
Weight, g	-	30.0	-	-	30.0	30.0	-	-	30.0	30.0	30.0	-
Products recovered												
Conc., % H_3PO_4	14.9	14.3	2.4	22.9	22.5	19.2	9.0	29.1	29.1	25.8	21.8	12.5
Weight, g	43	16.2	68.4	18.4	24.4	28.0	-	21.1	27.3	38.5	28.7	-
% of input[a]	61.8	22.4	15.8	18.5	24.1	23.7	33.7[b]	15.2	19.6	24.6	15.5	25.1[b]

[a] Total input based on H_3PO_4 in initial acid and washes.

[b] Calculation based on H_3PO_4 input less that recovered as product and wash liquors.

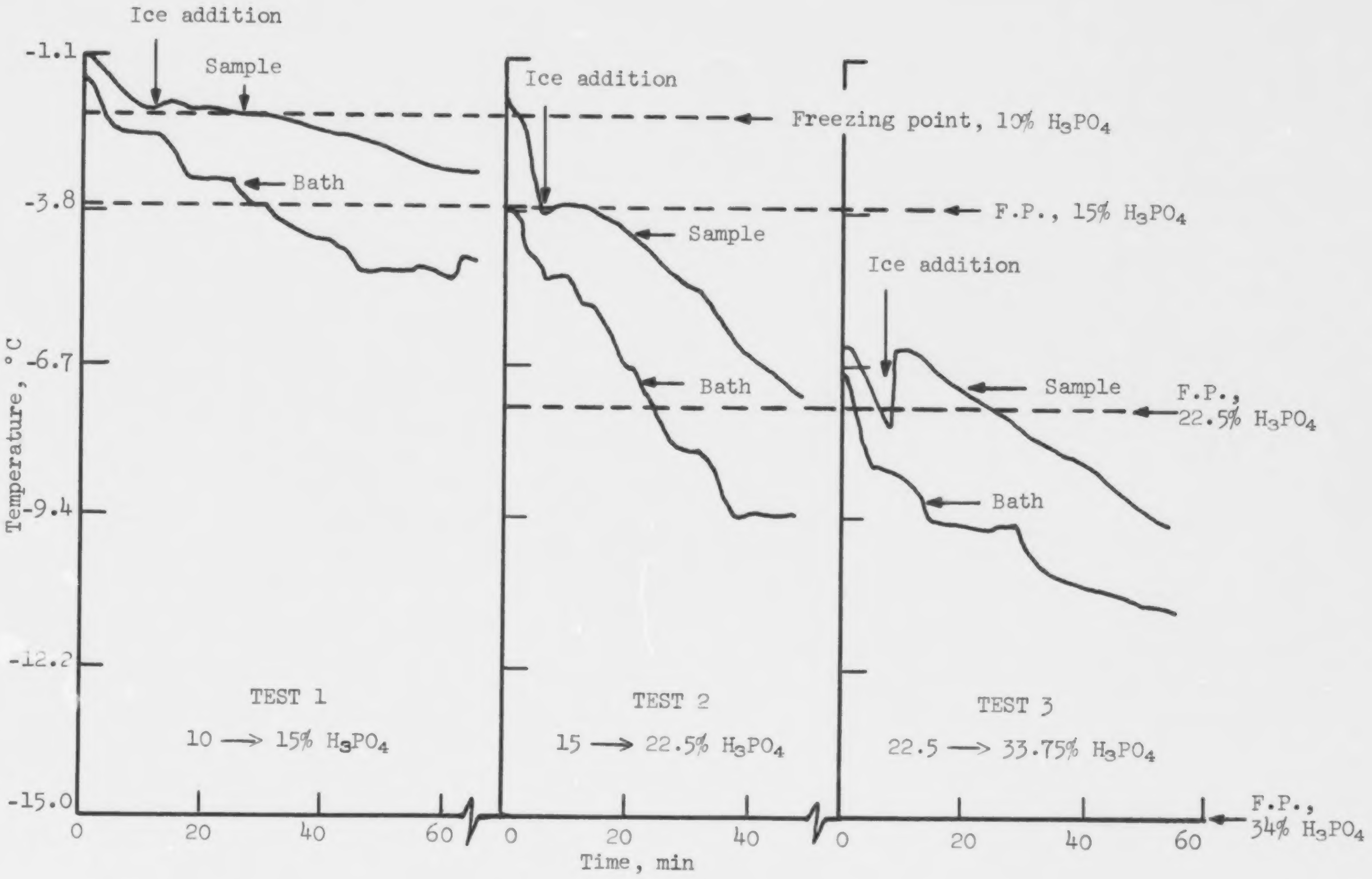


Figure 28. Cooling curves for weak phosphoric acid samples in freeze-concentration tests.

and 15.8% was in the final cake. Obviously, a more strenuous washing procedure would be required, possibly one in which the cold water would be used in two or three countercurrent washing steps. The projected flowsheet (Figure 27) indicates two countercurrent wash steps. The low recovery of wash solution (16.2 g of 30 g input water) probably was due to the freezing of the wash water when it contacted the colder ice (-3°C). This illustrates a problem of operating the process in a batch manner; such problem should be nonexistent or greatly reduced with use of a continuous countercurrent washing procedure as discussed later.

Test 2 involved planned concentration from 15 to 22.5% H_3PO_4 using fresh acid feed. In this test, the acid was seeded at -3.72°C and was cooled to the planned -7.22°C. Filtration recovered 18.4 grams of 22.9% H_3PO_4; this low recovery (18.5%) may have been due to the higher viscosity of the acid which resulted in an increased interstitial liquor content. The ice cake then was washed, first with a solution containing 15.23% H_3PO_4 (the same concentration of acid as was the beginning material) and then with a wash containing 9.85% H_3PO_4 (the beginning material from the previous step) to simulate a countercurrent washing procedure as outlined in Figure 27. Filtrate from the first wash contained 24.4 grams of 22.5% H_3PO_4 and that from the second wash contained 28 grams of 19.2% H_3PO_4; both recoveries indicate the freezing of some water from the wash solution due to the low temperature of the ice. The final cake analyzed 9% H_3PO_4; it is noted that this cake was not water washed as it would be in the projected procedure outlined in Figure 27. Recoveries of phosphoric acid, based on total feed including that supplied in the wash solutions, were 18.5% in the strong acid filtrate, 24.1% in the first wash, and 23.7% in the second wash. Proportion remaining in the final cake was 33.7%.

Test 3 was made in a manner similar to test 2. Fresh input acid containing 24.45% H_3PO_4 (intended) was cooled rapidly to -6.22°C then seeded at -8.75°C and cooled slowly to -9.44°C. The large rise in temperature (Figure 28) on seeding may indicate that the input acid was more dilute than thought. Concentration to the intended 33.75% final acid concentration would have required cooling to about -15°C; however, the slurry became very thick at -9.44°C and concentration had to be stopped. Increased viscosity of the acid probably helped thicken the slurry. Filtration allowed collection of 21.1 grams of 29.1% H_3PO_4, washing with 30 grams of 22.45% H_3PO_4 allowed collection of an additional 27.3 grams of 29.1% H_3PO_4, washing again with 30 grams of 22.45% H_3PO_4 allowed collection of 38.5 grams of 25.8% H_3PO_4, and a third wash with 30 grams of 15.23% H_3PO_4 allowed collection of 28.7 grams of 21.8% H_3PO_4. The final cake contained 12.5% H_3PO_4; in the projected procedure (Figure 27) this cake would be further washed. Recovery of phosphoric acid, based on total feed including that supplied as wash solution, was as follows: 15.2% in strong acid filtrate, 19.6% in first wash, 24.6% in second wash, and 15.5% in third wash. Proportion remaining in the final cake was 25.1%.

Conclusions

Results of the present series of tests indicate generally the workability of a three-stage freeze concentration as outlined in Figure 27. Indications are, however, that final acid concentration might have to be limited to 30% or less, because of excessive thickening. Thickening might be greater also with wet-process acid containing impurities. The data are not sufficient to predict accurately the amount of acid that would remain in the ice discharged from the three-stage process. For application to acid from a steam-plant scrubber system, it might be feasible to recycle melted ice to the scrubber as makeup water and thus recover all the acid. It is noted that good insulation would have to be maintained to minimize the cost of refrigeration and to minimize loss of ice due to melting when washing with solutions that have been allowed to warm. Each solution would have to be maintained at a different temperature.

Consideration should be given to application of a fully continuous procedure. Such a process might suffice to concentrate wet-process acid to about 30% H_3PO_4 while eliminating the problem of transfer of ice countercurrently to the preceding stage for washing and control of multiple wash solutions at different temperatures. With the closer control possible with continuous countercurrent washing, it is likely that the P_2O_5 lost in the ice might be decreased significantly.

CONCENTRATION OF AMMONIUM PHOSPHATE SOLUTION BY FREEZING

In an alternative approach, it would be possible to neutralize dilute phosphoric acid with ammonia before concentration by freezing. One advantage that might result would be the removal of unwanted impurities from the acid by partial ammoniation. The impurities would be precipitated and removed by filtration or centrifuging; they would be utilized in the production of solid or suspension fertilizers. Concentration of the filtrate would result in liquid ammonium phosphate fertilizer of 7-21-0 or 8-24-0 grade. Another advantage would be lower corrosion rates in the concentration equipment as compared with the conventional evaporation process due to the lower temperature and neutralization of the acid. A diagram of such a process is shown in Figure 29.

Experimental Work

This approach was studied in the laboratory. The ammonium phosphate solution used in the tests was 4-13-0 grade made by ammoniation of diluted reagent-grade phosphoric acid (about 14% P_2O_5). Initial tests were made by cooling the liquid sufficiently to obtain about equal proportions (by volume) of solid and liquid phases, separating the mixture by filtration, and then repeating the operation with the liquid phase until a total of five separations had been made. These tests were intended to determine whether the nutrient concentration in commercial fertilizers could be reached by freeze concentration of dilute ammonium phosphate solution.

Results (Table 17) indicated that freeze concentration of ammonium phosphate liquid to commercial grade might be feasible; the grade attained was higher (8.5-27.8-0) than commercial ammonium orthophosphate solution (8-24-0). However, the ice purity was relatively poor and it decreased as the concentration ($N + P_2O_5$) of the liquid fraction from the separations increased. For example, the P_2O_5 content of the ice from the first separation (test 1) was 6%

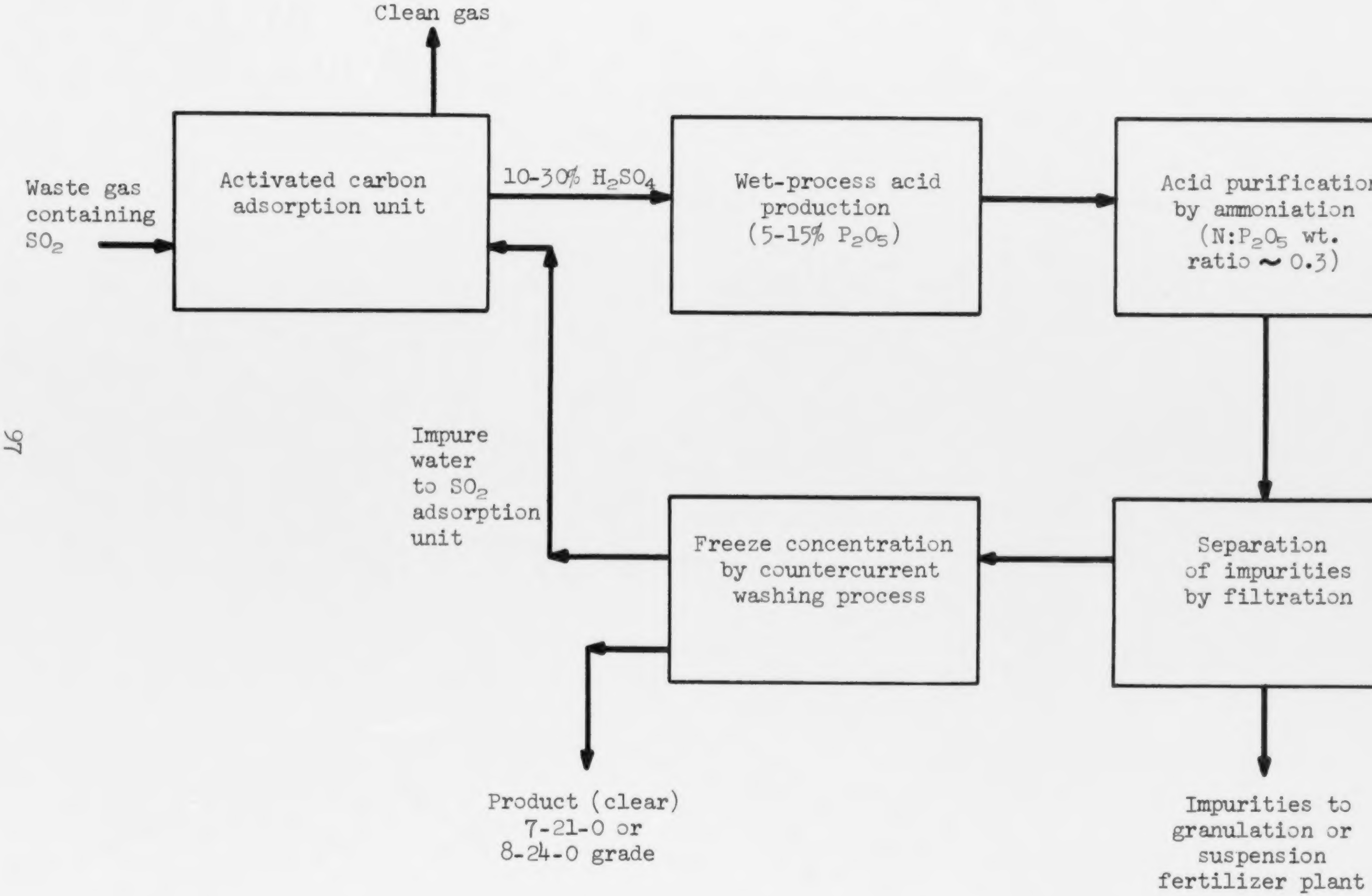

Clean gas
Waste gas containing SO_2
Activated carbon adsorption unit
10-30% H_2SO_4
Wet-process acid production (5-15% P_2O_5)
Acid purification by ammoniation ($N:P_2O_5$ wt. ratio ~ 0.3)
Impure water to SO_2 adsorption unit
Freeze concentration by countercurrent washing process
Separation of impurities by filtration
Product (clear) 7-21-0 or 8-24-0 grade
Impurities to granulation or suspension fertilizer plant

Figure 29. Utilization of sulfur dioxide from stack gas in production of ammonium phosphate liquid fertilizer--flow diagram.

TABLE 17. TESTS[a] OF FREEZE CONCENTRATION OF AMMONIATED PHOSPHORIC ACID SOLUTION[b]--TEST DATA

Test No.	Crystallization temp., -°C	Separation, % by wt.		Analysis, % in				Recovery, %
				Solid		Liquid		$N + P_2O_5$ in
		Solid	Liquid	N	P_2O_5	N	P_2O_5	liquid fraction
1	5.6	16	84	1.9	6.0	4.4[c]	14.4[c]	92.8
2	5.9	10	90	1.8	5.8	4.7[c]	15.3[c]	95.7
3	7.2	27	73	2.5	8.0	5.5[c]	18.1[c]	86.0
4	9.3	38	62	3.2	10.6	7.0[c]	22.7[c]	77.9
5	11.8	40	60	4.6	15.0	8.5[c]	27.8[c]	73.6

---

[a] Procedure: A 1000-gram batch of solution was placed in a closed container and then cooled to the temperature required to obtain an appreciable amount of solids which were separated by filtration. The procedure was repeated with the filtrate portion until five separations had been made.

[b] Starting liquid was 4-13-0 grade made by ammoniation of diluted reagent-grade phosphoric acid (14% P_2O_5).

[c] Calculated values.

as compared with 15% from the fifth separation (test 5). Guided by these results, tests were made to study procedures for increasing ice purity.

A series of exploratory tests was made to study the effect of water washing and of crushing the ice fraction prior to washing on the purity of recovered ice. The results of these tests are given in Table 18.

Water washing of the ice fraction was beneficial to the ice purity, and purity was further increased by crushing the ice prior to washing. Without water washing, the ice fraction obtained in crystallization at -5.6°C contained 5.2% P_2O_5 as compared with 3.7% with water washing of uncrushed ice; crushing of the ice resulted in a further increase in ice purity (contained only 2.8% P_2O_5).

In another series of tests, simulation of a continuous countercurrent washing procedure was studied. In this series of tests a batch of 4-13-0 grade liquid was cooled to the temperature required to obtain about equal proportions of solid (ice) and liquid phases, and then separated. The ice fraction from each separation was saved but allowed to melt and the procedure was repeated on the liquid phase for four additional times. Then the melted ice sample from the fifth separation was combined with the melted ice from the fourth separation, cooled to freeze out ice and separated; this ice fraction then was melted and combined with the melted ice from the third separation and the procedure was repeated until all of the previously saved ice samples had been processed. The ice from each separation was washed with a small amount of water (2% by wt. of total sample used in each separation). The results of these tests are given in Table 19.

The ice purity was increased appreciably with use of the simulated countercurrent procedure. In the four consecutive freeze-out operations, the purity of ice was increased from 2.7-7.8-0 to 0.31-0.95-0 grade. The liquid fraction from this ice (test 4) was 2.2-6.5-0 grade, which is half the concentration of the original starting solution (4-13-0 grade).

Conclusions

These results indicate that dilute ammonium phosphate solutions made and purified by ammoniation of dilute phosphoric acid produced from dilute sulfuric acid might be concentrated to usable grade by freeze concentration. Continuous countercurrent washing would be necessary, and more than one stage of this type of freeze concentration might be needed to attain the desired concentration gradient between the ice and the fertilizer product. However, the ice purity required in freeze desalination of water would not be needed since the melted ice could be used for recovery of the dilute sulfuric acid used in the proposed process.

TABLE 18. TESTS[a] OF FREEZE CONCENTRATION OF AMMONIATED PHOSPHORIC ACID SOLUTION--

EFFECT OF PROCEDURES OF SEPARATION ON PURITY OF SOLID (ICE) PHASE

		Freeze concentration data								
		Solid (ice) phase				Liquid phase				
		Melt (at 24°C),		% by wt.				% by wt.		P_2O_5
Test No.	Crystallization temp., -°C	sp. gr.	Wt. %	N	P_2O_5	Sp. gr. at 24°C	Wt. %	N	P_2O_5	recovery, %
Tests Made Without Water Washing of Solid (Ice) Phase										
1-1	5.6	1.040	15.3	1.6[b]	5.2	1.156	84.7	4.8	15.5[b]	94.3
1-2	6.7	1.056	22.9	2.2[b]	7.0	1.179	77.1	5.2[b]	17.0[b]	89.1
1-3	7.7	1.076	20.1	3.0[b]	9.8	1.198	79.5	6.0[b]	19.5[b]	88.7
1-4	9.7	1.112	34.1	3.9[b]	12.7	1.223	65.9	6.5[b]	21.1	76.2
1-5	11.7	1.192	27.8	6.0[b]	19.4	1.252	72.2	7.0[b]	22.8	75.3
Tests Made With Water Washing of Solid (Ice) Phase										
2-1	5.6	1.025	11.1	1.1	3.7	1.152	88.9	4.4[b]	14.3[b]	96.9
2-2	6.7	1.044	25.6	1.8	6.0	1.174	74.4	4.6[b]	15.0[b]	87.9
2-3	7.7	1.048	18.2	2.4	7.8	1.194	81.8	5.5[b]	18.0[b]	91.2
2-4	9.7	1.100	35.0	3.6	11.7	1.222	65.0	6.4[b]	20.7	76.7
2-5	11.7	1.132	20.8	4.4	14.4	1.248	79.2	7.0[b]	22.8	85.8
Tests Made With Water Washing of Crushed (Ice) Phase										
3-1	5.6	1.025	11.2	0.9	2.8	1.154	88.8	4.5	14.5[b]	97.7
3-2	6.7	1.024	20.9	1.3	4.3	1.178	79.1	5.0	16.3[b]	93.5
3-3	7.7	1.040	15.5	2.0	6.6	1.196	84.5	5.8	18.8[b]	93.9
3-4	9.7	1.116	31.0	3.4	11.0	1.223	69.0	6.5	21.2	81.1
3-5	11.7	1.155	22.2	3.1	10.1	1.251	77.8	7.1	23.1	88.9

[a] Procedure: Crystallization and separation were by the same procedure as described in Table 17. After separation the variations in washing of solid phases described were made (amount of wash was 2% of the total weight of the sample).

[b] Estimated analysis based on specific gravity of solution.

TABLE 19. SIMULATED COUNTERCURRENT WASHING PROCEDURE[a] FOR FREEZE CONCENTRATION OF LIQUID FERTILIZER

		Freeze concentration data								
			Solid (ice) phase				Liquid phase			
Test No.	Charge composition	Temp., -°C	Wt. %	Sp. gr. at 24°C	% N	% P_2O_5	Wt. %	Sp. gr. at 24°C	% N	% P_2O_5
1	i-4 (27.1)[b,c] + i-5 (38.9)[b,c]	3.3	32.7	-[d]	-[d]	-[d]	67.3	-[d]	-[d]	-[d]
2	No. 1[e] (21.6) + i-3 (65.4)	2.8	36.3	-[d]	-[d]	-[d]	63.7	1.080	-[d]	-[d]
3	No. 2[e] (32.3) + i-2 (132.8)	2.2	45.2	-[d]	-[d]	-[d]	54.8	1.075	-[d]	-[d]
4	No. 3[e] (73.3) + i-1 (235.3)	2.8	36.6	1.005	0.31	0.95	63.4	1.070	2.2	6.5

[a] A batch of nominal 4-13-0 grade liquid was cooled to the temperature required to obtain about equal proportions (by vol.) of solids and liquid, and then separated on a cooled, fritted glass filter. The solid phase (ice) was saved and the procedure was repeated with the liquid phase for four additional times to obtain a total of five ice samples (i-1, i-2, i-3, i-4, i-5) then countercurrent operation was carried out by combining i-5 and i-4, freezing, and separating. Ice from this separation was combined with i-3, cooled, and separated; this procedure was repeated until all of the previously saved ice samples were processed. Each of the ice separations was washed with a small amount of water (2% by wt. of total sample).

[b] The numbers shown in parentheses indicate the weight of mix, grams.

[c] Estimated grade of starting mixture (i-5 + i-4) was 2.7-7.8-0.

[d] Not determined.

[e] Ice from indicated test.

MELAMINE SCRUBBING

The Applied Research Branch assisted the Fundamental Research Branch in the study of a melamine scrubbing process (12) for the removal of sulfur dioxide from waste flue gases. Our work included tests with actual stack gas performed at the Colbert Steam Plant. As conceived, the process included the following steps:

1. Scrubbing SO_2- and SO_3-laden waste gas with an aqueous slurry of melamine.
2. Removing the spent slurry solids (primarily melamine sulfite and melamine sulfate adducts) from the liquid.
3. Recovering melamine from the above adducts by thermal decomposition of the melamine sulfite adduct.
4. Recovering melamine from the melamine sulfate adduct by chemical regeneration means as necessary. Use of ammonia as the regenerating chemical is suggested.
5. Return of the recovered melamine to the scrubber in slurry form.
6. Use of the sulfur dioxide released in the thermal regeneration step to produce sulfuric acid or other valuable sulfur-containing compounds in external units.
7. Use the sulfur trioxide recovered by chemical regeneration (when necessary) as a fertilizer or in fertilizer processes.

Two Fundamental Research Branch progress reports (August and December 1976) describe development work done on the project. The work done on the scrubbing step did not include the reuse of regenerated melamine, although both the scrubbing and regeneration steps were studied.

TESTS WITH SYNTHETIC GAS

Exploratory Tests

Initially, a few exploratory tests were made to assist in defining the test parameters and procedures to be used at Colbert Steam Plant. In these tests the concentration of the melamine slurries was varied over the range 2 to 6%; use of 6% was adopted to increase the amount of filterable solids at the end of each test. The slurries were used to scrub simulated stack gas

(0.3% SO_2, 3% O_2, 16% CO_2, and balance N_2) at a flow of 1.5 liters per minute. At first, the scrubbing was done in standard 250-milliliter gas scrubbing bottles equipped with coarse, fritted-glass spargers. However, plugging due to the buildup of melamine sulfate was found to be a problem. Therefore, a 7-millimeter open-end glass tube was used as a sparger and this later was changed to a 10-millimeter open-end tube. Also, a 125-milliliter scrubber bottle was substituted to increase depth of submersion and contact time. However, when using 125-milliliter scrubbers, there was a tendency for the slurry to flow over to the next unit; therefore, for later tests the 250-milliliter scrubbers were used.

After completion of each test, the slurry was regenerated chemically by adding sodium hydroxide until the pH reached about 7. However, it was found that a near-neutral pH resulted in the formation of melamine sulfite adducts with melamine to sulfurous acid mole ratio greater than 2, indicating less than complete regeneration, so in later tests an excess of base was added during chemical regeneration. After regeneration, the solids were removed by filtration and the scrubber mother liquor was used to reslurry the regenerated solids. This was done to minimize melamine losses due to solubility in the scrubbing liquor.

Process Tests

Planned startup of the Colbert limestone scrubber pilot plant (on which availability of stack gas for the melamine scrubbing tests depended) was delayed; therefore, on completion of the exploratory tests discussed above, it was decided to test the melamine process in its full cyclic mode using synthetic stack gas, prior to the tests at Colbert.

Four 250-milliliter gas-scrubbing bottles numbered 1 through 4 were used, each with 10-millimeter open-tube gas inlet. Each scrubber bottle was charged with a slurry of melamine that consisted of 6.0 grams of reagent-grade melamine and 100 milliliters of scrubber liquor (approximately saturated with melamine sulfite) from previous exploratory tests. The scrubbing train consisted of three of these scrubbing bottles in series (positions I, II, III), and the unused bottle was regenerated while the other three were in use. Gas, simulating stack gas except for oxygen content, was delivered to the scrubber bottle in position I at a rate of 1.5 liters per minute. The gas contained 0.32% SO_2, 19.4% CO_2, and 80.3% N_2; oxygen was omitted to avoid possible oxidation problems in these preliminary tests. Immediately following the scrubber bottle in position I, a glass tee and stopcock were used to divert 100 milliliters per minute of the off-gases through a calcium sulfate drying tower and a Manostat flowmeter to an ultraviolet spectrophotometer. The remaining 1.4 liters per minute of off-gases was delivered to the bottle in position II, and thence to the last scrubber (position III). The fourth scrubber was held in reserve for addition to the system later, as discussed below.

In operation, when SO_2 content of the off-gases from scrubber bottle in position I reached 50% of the level in the inlet gas (50% breakthrough) as measured by the UV spectrophotometer, that scrubber bottle was removed for regeneration and the other bottles were advanced from position II to position I and from position III to position II. The reserve scrubber bottle then was added to the system in position III. At the next 50% breakthrough, the same procedure was followed, with the regenerated scrubber bottle being placed back in the system in position III. These cycles were repeated until each scrubber bottle had been regenerated and returned to the system four times.

Two methods of regeneration were used--thermal and chemical. Scrubber bottles 1, 2, and 3 were always regenerated by filtration and heating (200°C) of the solids to volatilize the absorbed SO_2 and H_2O. This thermal regeneration was carried out in a glass-enclosed vessel which allowed the use of N_2 (100 ml/min) as a sweep gas over the surface of the solids. Scrubber bottle 4 always was regenerated chemically by filtration and leaching of the solids with an excess of ammonium hydroxide (25 ml of 12% NH_4OH solution) to remove both SO_2 and SO_3 in addition to the absorbed water. After regeneration (either thermal or chemical), the solids were recombined with their filtrates and adjusted to their initial slurry volume using water.

It was observed that after filtering the spent slurry a precipitate formed in the clear liquor. In one case, this precipitate was removed by filtration; its dry weight was about 0.6 gram. On further standing of the filtrate at ambient temperature, more of the precipitate formed. Microscopic examination later showed that the separated portion of the precipitate had the optical properties of a compound which was reported to be $(C_3H_6N_6)_2 \cdot H_2SO_4$. Because of the amount of time required for removal and the relatively small amount of precipitate (0.6 g), it was decided that only one filtration would be made on each slurry and that any later precipitate would be left in the liquor.

The results of the tests are shown in Table 20 and Figures 30 and 31. Typical data on the concentration of SO_2 in the exit gas from the position I (first stage) scrubber (Figure 30) show that the melamine absorbed all of the inlet SO_2 for an average of 87 minutes each cycle or 82% of the total scrubbing time. At that time, scrubbing efficiency dropped quite abruptly, and SO_2 concentration in the off-gas rose quickly to 50% of the inlet concentration.

The weight of SO_2 absorbed by each scrubber bottle for each of the four cycles is shown in Figure 31. The average amounts of SO_2 removed per scrubber bottle were 1.60, 1.48, 1.36, and 1.37 grams for cycles 1 through 4, respectively. The decrease in scrubbing capacity for additional cycles most likely is attributable to oxidation of melamine sulfite to the sulfate form (which cannot be regenerated thermally) and to mechanical losses in the regeneration procedure. The high value for scrubber bottle 4 in the second cycle was a result of the greater scrubbing capacity of a slurry of 6 grams of fresh melamine in distilled water which replaced the original scrubber slurry which was inadvertently destroyed during regeneration after the first cycle. The low values for scrubber bottles 1 and 2 in the second cycle probably were due to shorter times used in regeneration after the first cycle. Regeneration time at 200°C for bottles 1 and 2 after the first cycle was 30 and 40 minutes, respectively, but was increased to 80 minutes after additional cycles.

TABLE 20. REMOVAL OF SULFUR OXIDES FROM WASTE GASES[a] BY MELAMINE SCRUBBING (LABORATORY TEST DATA)

Cycle[b]	Scrubber bottle No. 1				Scrubber bottle No. 2				Scrubber bottle No. 3				Scrubber bottle No. 4			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Initial slurry																
Wt. melamine, g	6.0				6.0				6.0				6.0	6.0		
Wt. liquor, g[c]	100.15				99.9				99.7				99.1	100[c]		
Final slurry																
Time to 50% breakthrough, min	131	96.5	100	101	122	86	105	92	105	109	98	102	109.5	138	91	104
pH	3.1	2.8	3.1	3.1	3.0	3.1	3.1	3.1	3.0	2.9	2.2	-	3.1	2.7	3.0	3.1
Wt. slurry, g	103.85	103.95	102.65	102.75	103.5	104.4	103.1	104.1	103.7	103.2	103.0	103.8	103.0	103.5	104.0	102.9
Wt. solids, g[d]	10.135	10.19	9.43	10.7	10.48	10.35	8.9	11.6	9.66	10.96	8.74	10.88	-	8.54	9.06	8.55
Wt. loss, % of input	2.2	2.1	2.8	2.7	2.3	1.4	2.4	1.7	1.9	2.1	2.1	1.8	2.0	2.4	1.9	2.1
Regeneration																
Time at 200°C, min	30	80	90	80	40	80	80	80	50	80	80	80				
Volume NH_4OH (12%), ml														25.0	25.0	25.0
Wt. regenerated solids, g	5.70	5.50	5.25	5.07	5.97	5.66	5.43	5.43	5.71	5.50	5.31	5.12		4.98	5.19	5.12
Wt. regenerated slurry, g	94.25	95.35	117.45		95.1	95.4	85.7		96.1	93.3	97.8			96.2	95.0	
Wt. H_2O added, g[e]	11.9	10.3	10.2		10.8	10.2	20.2		9.3	11.9	7.9			9.8	10.1	
Average SO_2 concentration of inlet gas, ppm	3174	3207	3213	3213	3174	3233	3279	3246	3266	3226	3220	3193	3266	3207	3180	3161
SO_2 removal, % of input[f]	97.5	95.4	98.2	97.8	97.2	93.2	97.2	97.5	93.5	97.6	97.4	95.9	96.5	98.3	97.5	97.6
Weight SO_2 removed, g	1.74	1.32	1.38	1.39	1.65	1.17	1.46	1.28	1.42	1.55	1.36	1.37	1.57	1.90	1.24	1.43
Mole ratio																
$\frac{\text{Moles } SO_2 \text{ scrubbed}^g}{\text{Moles input melamine}}$	0.569	0.456	0.495	0.522	0.542	0.385	0.508	0.462	0.466	0.534	0.486	0.508	0.515	0.622	0.491	0.541

[a] Simulated span gas: 0.32% SO_2, 19.4% CO_2, 80.3% N_2 at a flow of 1.5 l/min.

[b] Cycle consisted of bottle being operated successively in scrubber positions III, II, and I (until 50% breakthrough), then regenerated.

[c] Liquor was from previous exploratory tests, approximately saturated with melamine sulfite (slurry from scrubber bottle No. 4 was lost and replaced with 6 g melamine in 100 g water after first cycle).

[d] Ethanol-washed and air-dried.

[e] Added to maintain volume of initial slurry.

[f] Removal by scrubber bottle while operating in scrubber position I (first stage). Calculated from UV spectrophotometer chart areas.

[g] Assuming all of regenerated scrubber solids were melamine.

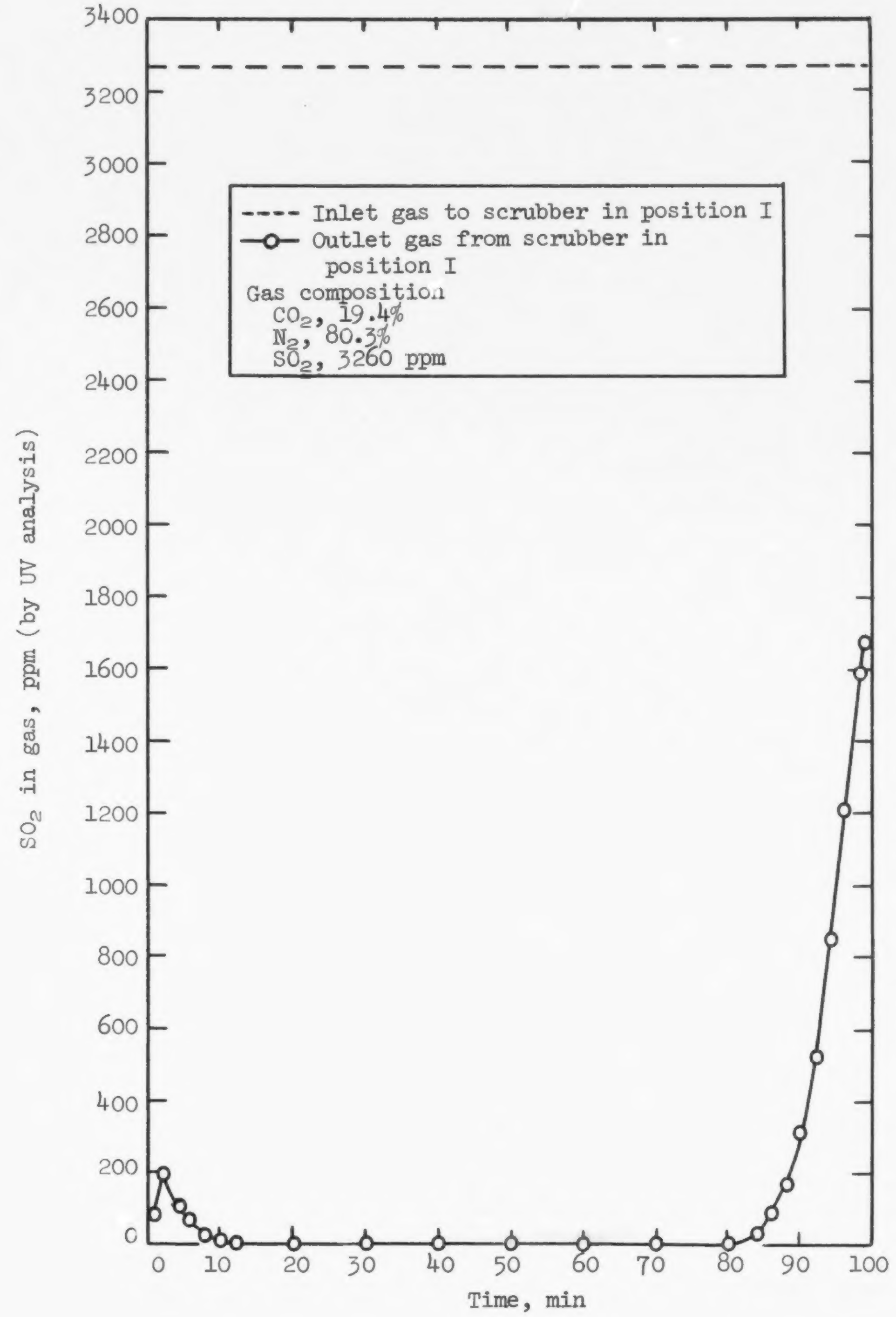
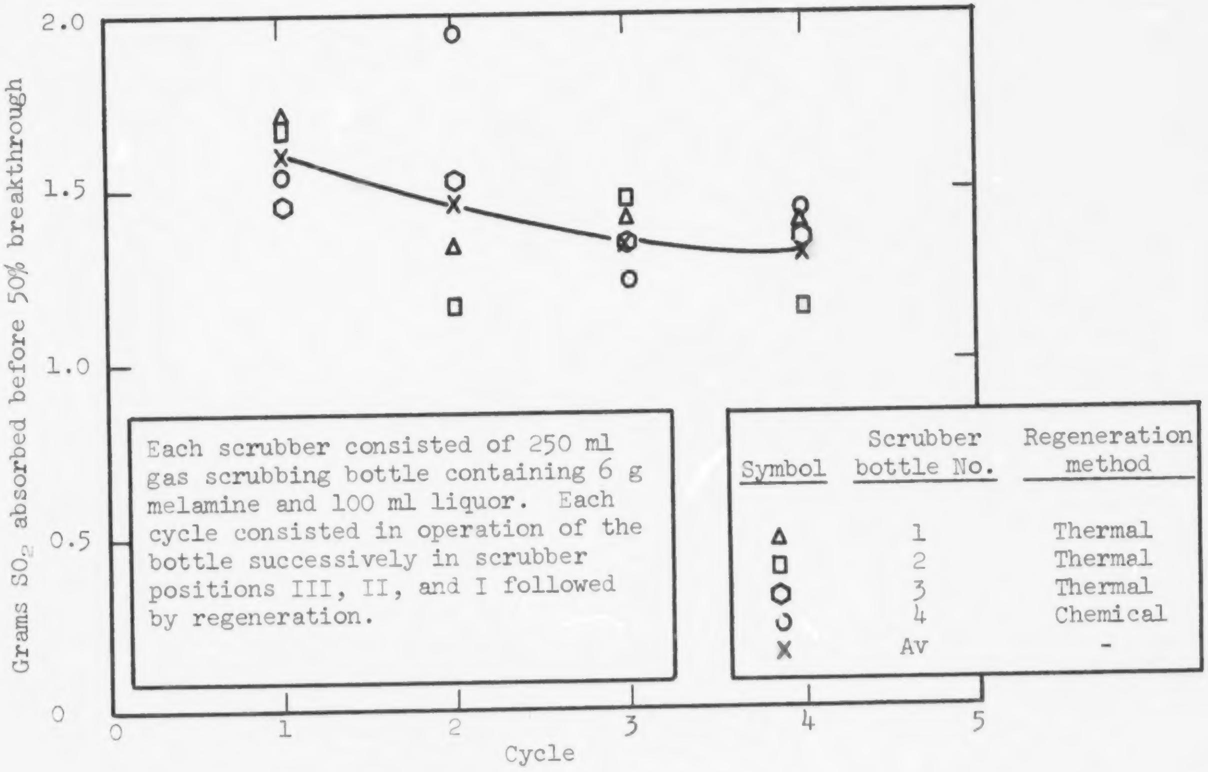


Figure 30. Laboratory removal of SO_2 from synthetic gas by scrubbing with melamine slurry--typical analyses of gases at inlet and outlet of first scrubber versus time.



Each scrubber consisted of 250 ml gas scrubbing bottle containing 6 g melamine and 100 ml liquor. Each cycle consisted in operation of the bottle successively in scrubber positions III, II, and I followed by regeneration.

Symbol	Scrubber bottle No.	Regeneration method
△	1	Thermal
□	2	Thermal
⬡	3	Thermal
○	4	Chemical
×	Av	-

Figure 31. Laboratory removal of SO_2 from synthetic gas by scrubbing with melamine slurry--effects of regeneration on absorption of SO_2.

Chemical analysis of the regenerated scrubber solids showed that bottles 1, 2, and 3 (thermal regeneration) were regenerated to 86.7% of their theoretical scrubbing capacity /assuming formation of the $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot nH_2O$ salt/ after four cycles. In these bottles, 89.6% of the sulfur that was not regenerated was in the oxidized (sulfate) form, which is equivalent to an average of 0.019 gram of sulfur oxidized per regeneration. This is equivalent to 1.3% of the sulfur absorbed. Bottle 4 (chemical regeneration) was regenerated to 99.2% of its theoretical scrubbing capacity with none of the remaining sulfur in the sulfate form after the fourth cycle. After the test, recovery of melamine used in all four of the bottles amounted to only an average of 82.8% of the input. This probably was due to mechanical losses from the small quantities of materials that had to be handled.

It was concluded from this test that 100 milliliters of a 6% slurry of melamine used in each of four scrubbers would allow sufficient scrubbing capacity so that any one scrubber could be regenerated while the others removed all of the inlet SO_2 even as the buildup of sulfate became critical. Further, it was determined that thermal regneration of the sulfite sulfur in the solids would be essentially complete after 80 minutes at 200°C as evidenced by the lack of acidic gases in the sweep gas used. However, if a large degree of oxidation occurs, a longer heating time may be required since the presence of sulfate inhibits the volatilization of the sulfite sulfur. With the presence of oxygen in actual stack gas (about 5% O_2) it is expected that oxidation will be greater.

TESTS WITH COLBERT STEAM PLANT GAS

The tests were made using stack gas from Colbert units 3 and 4. The SO_2 content of the gas varied from 2000 to 2900 ppm and the oxygen content varied from 7 to 10.5%. Cyclic tests were made in which melamine slurry was first used to scrub the gas and then the spent melamine was regenerated and returned to the scrubbers. Tests were made to determine the effects of using a water-prescrubber and of the addition of an antioxidant to the scrubber slurry. As discussed previously, two methods of regeneration of the spent melamine were used, thermal and chemical. Thermal regeneration may be used to drive off absorbed water and sulfite sulfur but does not drive off any sulfate sulfur; temperatures as low as 200°C are suitable for thermal regeneration. Chemical regeneration, such as reaction with ammonium hydroxide, removes both sulfite and sulfate sulfur from the melamine, but the absorbent is somewhat soluble in the regenerating solution, which increases losses.

Equipment and Procedure

A series of four tests was made at the conditions tabulated below:

Test No.	Gas rate, l/min	Prescrubber in system	Antioxidant in slurry[a]	Scrubber temp., °C
1	2	No	No	52
2	2	No	Yes	52
3	2	Yes	No	52
4	2	Yes	Yes	52

a. 0.1% p-phenylenediamine added to original slurry.

As in the previous tests, four 250-milliliter gas-scrubbing bottles numbered 1 through 4 were used, each with 10-millimeter open-tube gas inlet. Each scrubber bottle was charged with a slurry of melamine that consisted of 6.0 grams of reagent-grade melamine and 100 milliliters of water saturated with melamine. The scrubbing train consisted of three of these scrubbing bottles in series (positions I, II, III), and the unused bottle was regenerated while the other three were in use. The equipment arrangement was as shown in Figure 32. Three of the four scrubber bottles (and the prescrubber, when in use) were placed in a water bath maintained at 52°C. Stack gas was drawn serially through the scrubbers and a condenser by pump No. 1 and was metered at the pump exit. The condenser was used to dry the gas enough to meter it. A second pump (pump No. 2; Figure 32) was used to pump as much gas as was possible (about 1.5 l/min) to exhaust; this was done to keep the flow in the incoming line as great as possible to prevent settling of fly ash in the lines and to prevent cooling and settling of the incoming gas as much as possible. The incoming line was a steam-traced 0.6-centimeter (1/4-in) stainless steel tube. Separate inlet streams from points upstream of the scrubber train and downstream of the first scrubber were passed through UV analyzers (Figure 32) to determine the SO_2 content of the gas at these points; these streams were passed through tubes filled with anhydrous calcium sulfate to remove water and any fly ash prior to entry to the UV cells. The stream originating between scrubbers 1 and 2 was metered as was the stream passing completely through the scrubber train; the total of these two metered rates was the rate of gas passing through scrubber 1.

In operation, when SO_2 content of the off-gases from the scrubber bottle position I reached about 50% of the level in the inlet gas (50% breakthrough) as measured by the UV spectrophotometers (about 1300 ppm at UV-2), that scrubber bottle was removed for regeneration and the other bottles were advanced from position II to position I and from position III to position II. The reserve scrubber bottle then was added to the system in position III. At the next 50% breakthrough, the same procedure was followed, with the regenerated scrubber bottle being placed back in the system in position III. These cycles were repeated until there was significant reduction in the effectiveness of the recycled melamine slurry or until four scrubbing cycles with each scrubber bottle had been completed. The melamine was not regenerated after the last cycle for each scrubber bottle.

Thermal regeneration is depicted in Figure 33. The first three of the four scrubbing bottles (bottle Nos. 1, 2, and 3) were subjected to thermal regeneration. Spent scrubber slurry was filtered on a coarse-fritted crucible and the solids, still on the filter, were placed in a closed glass vessel with

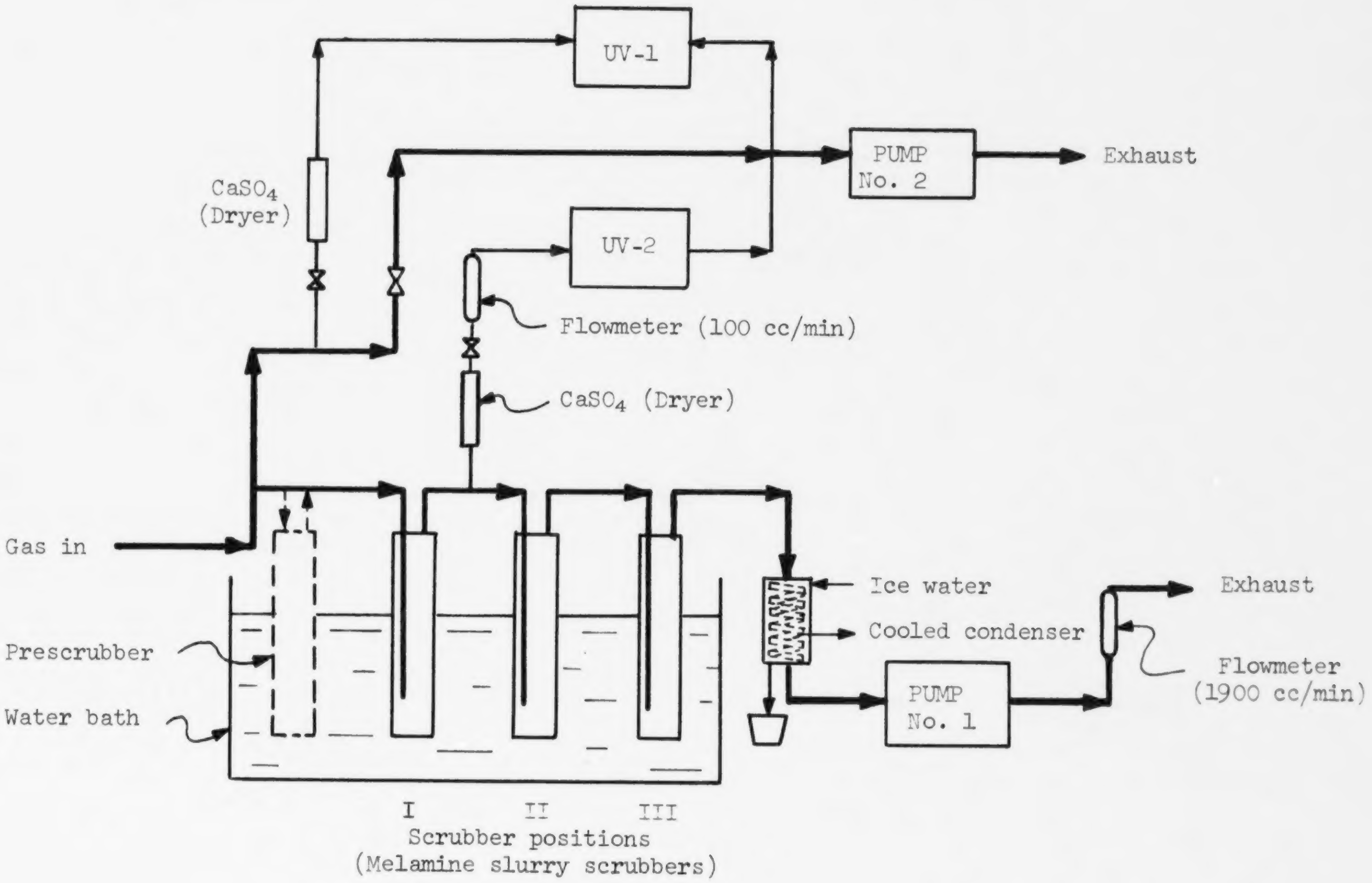

UV-1
CaSO$_4$ (Dryer)
PUMP No. 2
Exhaust
UV-2
Flowmeter (100 cc/min)
CaSO$_4$ (Dryer)
Gas in
Ice water
Cooled condenser
Exhaust
Prescrubber
Flowmeter (1900 cc/min)
PUMP No. 1
Water bath
I
II
III
Scrubber positions
(Melamine slurry scrubbers)

Figure 32. Equipment arrangement used in tests of melamine scrubbing of Colbert Steam Plant stack gas.

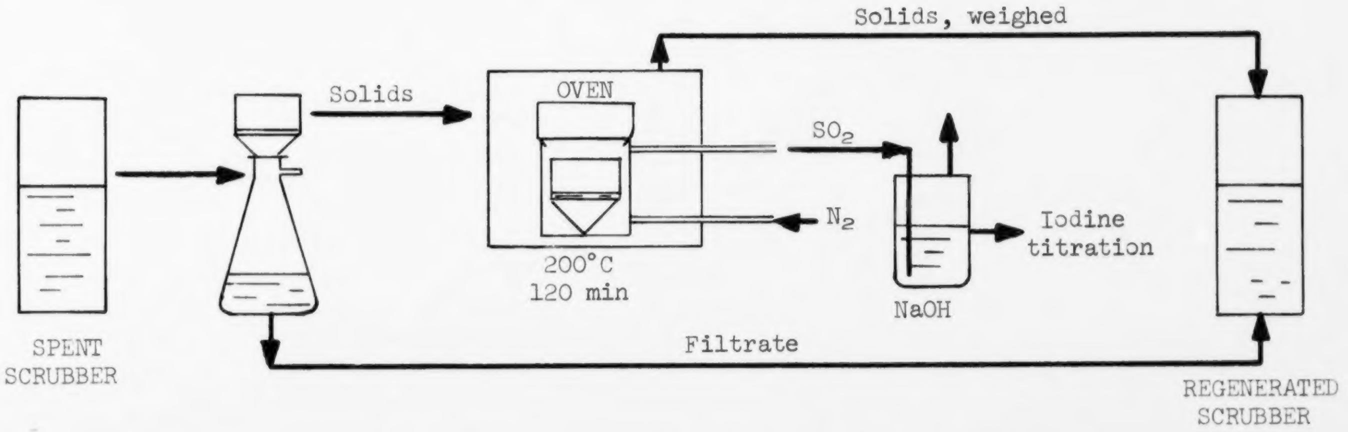

Solids, weighed
Solids
OVEN
SO_2
N_2
200°C
120 min
Iodine titration
NaOH
SPENT SCRUBBER
Filtrate
REGENERATED SCRUBBER

Figure 33. Thermal regeneration of spent melamine slurry.

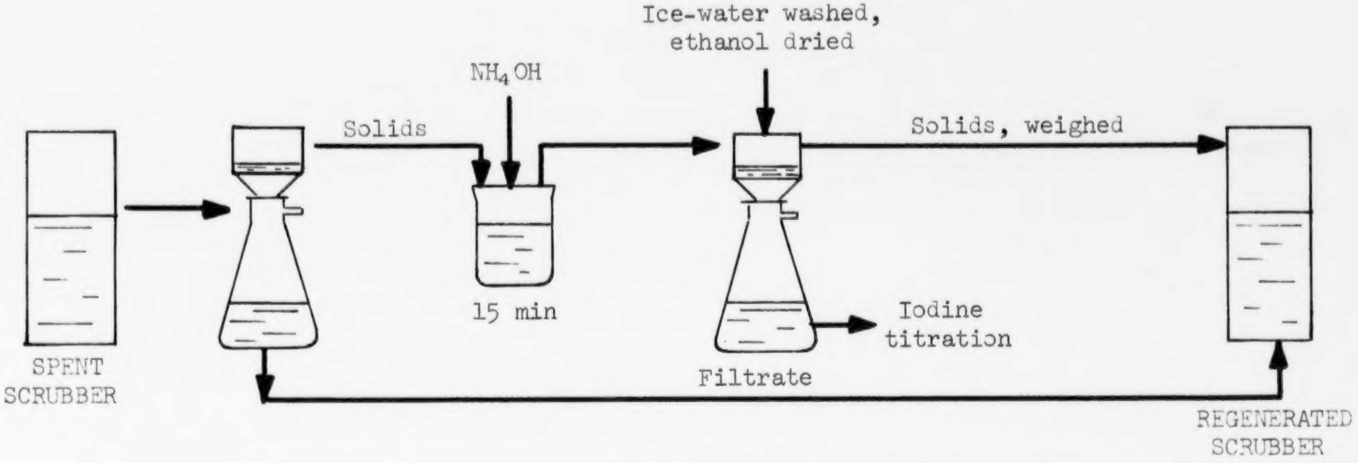

Ice-water washed, ethanol dried
NH_4OH
Solids
Solids, weighed
15 min
Iodine titration
SPENT SCRUBBER
Filtrate
REGENERATED SCRUBBER

Figure 34. Chemical regeneration of spent melamine slurry.

gas entry and delivery tubes attached. The solids in their container were placed in an oven held at 200°C for a period of 2 hours during which time the melamine sulfite was decomposed. A flow of nitrogen was passed through the vessel during regeneration to sweep out any released H_2O and SO_2 and to carry it into a sodium hydroxide solution to absorb the SO_2. This solution later was analyzed for SO_2 content by iodine titration. The regenerated melamine was weighed and recombined with the filtrate from the spent scrubber slurry to form the regenerated scrubber slurry. Any volume loss resulting from the scrubbing or regeneration steps was made up as water saturated with melamine at room temperature.

Chemical regeneration is depicted in Figure 34. Scrubber bottle No. 4 was subjected to this type regeneration. Spent scrubber slurry was filtered on a 30-milliliter coarse-fritted crucible and the solids were transferred to a 50-milliliter beaker where they were stirred in 25 milliliters of 12.5% NH_4OH solution for 15 minutes. The solids then were refiltered on the same crucible, washed with ice water five times (5 ml each wash), and then were washed with ethanol and air dried before weighing and recombining with the filtrate from the spent scrubber slurry. The regenerated scrubber slurry was brought back to its initial volume by the addition of water saturated with melamine. The filtrate from the ammonia reaction slurry was analyzed for sulfite sulfur by iodine titration during the tests and was later analyzed for total sulfur, total nitrogen, and ammoniacal nitrogen.

Discussion of Test Results

Data collected during the tests and indices calculated from these data are given in Table 21. Sulfur dioxide absorption by the individual scrubbers is shown in Figure 35, and recovery of SO_2 in the regeneration step is shown in Figure 36. The theoretical amount of SO_2 that could have been absorbed by the solid melamine in each scrubber would be about 1.52 grams according to the equation:

$$2C_3N_6H_6 + SO_2 + (1+x)H_2O \longrightarrow (C_3N_6H_6)_2 \cdot H_2SO_3 \cdot xH_2O$$

The melamine in solution would absorb about an additional 0.1 gram and the water could hold about 0.1 gram more so that the total SO_2 holding power of the individual scrubber would be about 1.7 grams. The amount of SO_2 absorbed in each scrubber includes that collected while that scrubber was in position I in the series plus that collected while it was in position II (breakthrough from scrubber in position I) and position III. These amounts were calculated from the input analysis and flow and from integration of the UV analyzer charts (SO_2 analysis). The values as calculated above are shown in Figure 35. They generally are higher for the first cycle than would be indicated by the original capacity of the scrubbers or by the amounts of SO_2 liberated during regeneration. No explanation of this inconsistency is offered. Errors in analytical values and in measured flows would not seem to account for the differences, particularly since the values for the second and succeeding cycles are much more reasonable than those for the first cycle. It is possible that there was some component of the stack gas which, when wetted

TABLE 21. REMOVAL OF SULFUR OXIDES FROM WASTE GASES BY MELAMINE SCRUBBING
(DATA FROM LABORATORY-SCALE TESTS AT COLBERT STEAM PLANT)

	Test 1				Test 2				Test 3				Test 4			
Prescrubber used?	No				No				Yes				Yes			
Scrubber bottle No.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Cycle 1^{a}																
Input SO_2, ppm^{b}	2492	2085	2439	2446	2318	2279	2405	2476	2432	2600	2550	2538	2584	2715	2570	2626
Input O_2, %^{c}	9.6	-	7.5	8.0	10.5	8.5	9.0	7.5	8.1	8.0	8.7	7.1	7.8	7.5	7.3	7.4
Initial slurry, g																
Melamine	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Para-phenylenediamine	0	0	0	0	0.1	0.1	0.1	0.1	0	0	0	0	0.1	0.1	0.1	0.1
H_2O^{d}	100	100	100	100	125	125	125	125	125	125	125	125	125	125	125	125
Time to 50% breakthrough, min	186.5	161.5	121	100	207	156	157	157	173	143	156	151	181	156	167	161
Total SO_2 fed, g^{e}	2.654	1.923	1.685	1.397	2.740	2.030	2.156	2.220	2.403	2.123	2.272	2.189	2.671	2.419	2.451	2.415
Removal of SO_2, %^{e}	97.4	96.1	94.4	96.7	95.7	97.0	95.7	96.4	96.0	96.4	97.6	96.1	96.8	94.6	96.6	95.7
SO_2 absorbed, g^{f}	2.582	1.914	1.662	1.441	2.623	2.081	2.122	2.228	2.307	2.138	2.290	2.155	2.586	2.369	2.492	2.390
Solids before regeneration, g	9.75	14.45	9.2	10.9	8.2	8.9	8.85	10.15	8.55	8.0	10.55	9.3	9.8	8.55	8.4	8.9
Regenerated solids, g	5.65	6.15	5.9	5.7	4.95	5.6	5.45	6.4	5.55	5.0	6.45	5.45	5.3	5.4	5.5	5.25
Indicated SO_2 regenerated, g	1.118^{g}	0.959^{g}	1.078^{g}	0.959^{h}	1.205^{g}	1.318^{g}	1.276^{g}	1.267^{h}	1.172^{g}	1.097^{g}	1.209^{g}	1.2[illegible]^{h}	1.298^{g}	1.238^{g}	1.231^{g}	1.268^{h}
Indicated SO_2 regenerated, %^{i}	43.3	50.1	64.9	66.6	45.9	63.3	60.1	56.9	50.8	51.3	52.8	58.2	50.2	52.3	49.4	53.1
Cycle 2^{a}																
Input SO_2, ppm^{b}	2525	2623	2492	2590	2297	2256	2522	2360	2509	2308	2742	2883	2566	2816	2808	2869
Input O_2, %^{c}	-	7.0	7.0	8.5	8.5	-	9.5	9.0	8.5	-	7.5	-	7.0	7.3	7.3	7.0
Recycled solids, g	5.65	6.15	5.9	5.7	4.95	5.6	5.45	6.4	5.55	5.0	6.45	5.45	5.3	5.4	5.5	5.25
Recycled slurry, g	104.9	92.8	91.9	95.5	118.9	110.1	114.7	113.6	121.8	115.2	121.7	17.1	124.5	127.0	125.2	121.5
H_2O added, g^{d}	0.7	12.6	13.6	10.2	12.3	20.6	16.3	17.4	9.3	15.4	9.1	13.9	7.0	3.9	5.8	9.8
Time to 50% breakthrough, min	73	74	70	116.5	109	119	103	112.5	98	114.5	82	94.5	105	99	102	92
Total SO_2 fed, g^{e}	1.053	1.109	0.996	1.723	1.430	1.533	1.484	1.523	1.404	1.509	1.284	1.556	1.539	1.592	1.636	1.507
Removal of SO_2, %^{e}	93.5	94.5	88.9	87.8	92.9	90.9	94.5	92.5	93.4	88.5	98.9	93.1	93.8	95.1	94.9	93.9
SO_2 absorbed, g^{f}	1.028	1.055	0.998	1.618	1.404	1.490	1.534	1.486	1.393	1.424	1.435	1.462	1.542	1.605	1.626	1.495
Solids before regeneration, g	16.0	10.35	16.5	18.8	9.55	10.5	10.15	10.4	12.95	11.2	10.55	9.3	12.0	10.7	11.0	10.5
Regenerated solids, g	7.2	6.85	6.7	6.0	5.25	5.3	5.6	5.1	6.6	6.3	6.45	5.45	5.55	5.8	5.5	5.05
Indicated SO_2 regenerated, g	0.518^{g}	0.375^{g}	0.556^{g}	0.788^{h}	1.177^{g}	1.156^{g}	1.252^{g}	1.219^{h}	0.749^{g}	0.915^{g}	0.742^{g}	1.168^{h}	1.243^{g}	1.277^{g}	1.230^{g}	1.213^{h}
Indicated SO_2 regenerated, %^{i}	50.4	35.5	55.7	48.7	83.8	77.6	81.6	82.0	53.8	64.3	51.7	79.9	80.6	79.6	75.6	81.1

[a] Cycle consisted of bottle being operated successively in scrubber positions III, II, and I (until 50% breakthrough), then regenerated.
[b] Inlet SO_2 measured with Perkin Elmer (Coleman 124-D) UV analyzer averaged for duration of test. Gas from Colbert units 3 and 4.
[c] Oxygen content of off-gas as measured before and after the test using Fyrite analyzer and averaged.
[d] Water saturated with melamine at room temperature.
[e] Calculated by integration of UV analyzer recorder charts, assuming constant flow of 2 l/min of gas through scrubber; feed includes SO_2 breakthrough from previous stage.
[f] Includes breakthrough area while scrubber was in position II of scrubbing cycle.
[g] Sulfur dioxide evolved during regeneration was absorbed in NaOH (3.8 g NaOH/100 g H_2O) and analyzed by iodine titration.
[h] Sulfur dioxide in filtrate from chemical regeneration of solids with 25 ml of 12% NH_4OH, filtered to recover solids for recycle and solids washed with five 5-ml portions of ice water, does not include sulfate sulfur.
[i] 100(SO_2 absorbed - SO_2 regenerated)/SO_2 absorbed.

(continued)

TABLE 21 (continued)

	Test 1				Test 2				Test 3				Test 4			
Prescrubber used?	No				No				Yes				Yes			
Scrubber bottle No.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Cycle 3^{a}																
Input SO_2, ppm^{b}	2557	2721	2623	2623	2254	2597	2573	2458	2849	2794	2492	2687	2877	2887	2327	2278
Input O_2, %^{c}	8.0	8.5	-	8.2	8.0	9.7	8.7	8.6	7.1	-	7.0	7.5	7.0	7.0	9.4	9.4
Recycled solids, g	7.2	6.85	6.7	6.0	5.25	5.3	5.6	5.1	6.6	6.3	6.45	5.45	5.55	5.8	5.5	5.05
Recycled slurry, g	89.5	94.8	87.1	86.5	118.0	116.6	112.9	109.9	128.2	124.5	126.5	120.8	120.5	125.5	128.6	124.2
H_2O added, g^{d}	40.0^{j}	35.7^{j}	43.3^{j}	44.2^{j}	13.2	14.1	18.1	21.1	2.9	6.1	4.4	10.2	11.0	5.4	2.4	7.1
Time to 50% breakthrough, min	17	40	60	103	110	101	109	108	75	82	77	87	101	100	125	126
Total SO_2 fed, g^{e}	0.248	0.622	0.914	1.543	1.416	1.498	1.602	1.516	1.220	1.308	1.096	1.335	1.660	1.665	1.648	1.639
Removal of SO_2, %^{e}	72.2	91.1	89.4	90.8	92.2	93.2	91.0	93.2	94.6	95.6	92.1	94.0	95.5	95.4	88.0	88.8
SO_2 absorbed, g^{f}	0.379	0.632	0.870	1.493	1.414	1.501	1.554	1.550	1.256	1.313	1.064	1.337	1.672	1.660	1.523	1.643
Solids before regeneration, g	11.3	15.65	14.1	-	11.2	9.7	8.3	10.0	14.95	15.4	13.75	13.9	12.8	12.6	12.9	10.8
Regenerated solids, g					5.55	5.1	5.45	4.75	7.0	6.8	6.85	4.9	5.65	5.5	5.55	4.70
Indicated SO_2 regenerated, g					1.156^{g}	1.068^{g}	1.116^{g}	1.124^{h}	0.546^{g}	0.716^{g}	0.663^{g}	0.883^{h}	1.205^{g}	1.145^{g}	1.183^{g}	1.119^{h}
Indicated SO_2 regenerated, %^{i}					81.8	71.1	71.8	72.5	43.5	54.5	62.3	66.0	72.1	69.0	77.7	68.1
Cycle 4^{a}																
Input SO_2, ppm^{b}					2425	2334	2329	2550	2633	2638	2702	2744	2280	2221	2203	2030
Input O_2, %^{c}					9.0	9.0	9.0-9.5	8.2	7.5	-	8.0	8.0	9.0	9.3	9.4	11.5
Recycled solids, g					5.55	5.1	5.45	4.75	7.0	6.8	6.85	4.9	5.65	5.5	5.55	4.70
Recycled slurry, g					120.3	112.2	114.5	113.8	125.3	119.3	123.4	115.3	122.7	122.5	120.0	126.6
H_2O added, g^{d}					10.9	18.5	17.4	17.2	5.8	11.3	7.5	15.7	8.8	8.4	11.0	4.7
Time to 50% breakthrough, min					94	105	108	95	55	69	57.5	101.5	125	126	147	252
Total SO_2 fed, g^{e}					1.302	1.400	1.437	1.384	0.827	1.040	0.887	1.591	1.628	1.598	1.490	2.922^{k}
Removal of SO_2, %^{e}					92.8	90.8	90.6	93.1	92.6	91.7	94.2	94.8	90.6	88.4	92.3	-
SO_2 absorbed, g^{f}					1.306	1.360	1.434	1.416	0.842	1.011	0.918	1.557	1.649	1.558	1.551	-
Final slurry, g	130.5	126.0	129.8	131.6	124.4	128.7	129.0	126.0	136.4	132.3	132.4	128.5	137.9	135.5	136.6	136.4
Final slurry pH	-	-	-	5.0^{l}	3.8	3.9	3.9	3.85	3.79	4.0	3.82	3.68	4.32	4.28	4.29	3.95
Weight dry solids recovered, g	7.4	8.3	7.6	8.0	7.75	7.65	7.60	6.55	8.65	8.40	8.95	7.45	10.05	12.6	15.3	9.5
Filtrate, ml	-	-	-	114	102	107	113	110	-	109	101	111	118	117	117	122
Filtrate, g	119.2^{m}	110.3^{m}	115.7^{m}	110.7	101.9	106.5	113.6	110.8	113.8^{m}	109.4	101.5	110.05	117.5	116.4	116.9	120.5

[a] Cycle consisted of bottle being operated successively in scrubber positions III, II, and I (until 50% breakthrough), then regenerated.

[b] Inlet SO_2 measured with Perkin Elmer (Coleman 124-D) UV analyzer averaged for duration of test. Gas from Colbert units 3 and 4.

[c] Oxygen content of off-gas as measured before and after the test using Fyrite analyzer and averaged.

[d] Water saturated with melamine at room temperature.

[e] Calculated by integration of UV analyzer recorder charts, assuming constant flow of 2 l/min of gas through scrubber; feed includes SO_2 breakthrough from previous stage.

[f] Includes breakthrough area while scrubber was in position II of scrubbing cycle.

[g] Sulfur dioxide evolved during regeneration was absorbed in NaOH (3.8 g NaOH/100 g H_2O) and analyzed by iodine titration.

[h] Sulfur dioxide in filtrate from chemical regeneration of solids with 25 ml of 12% NH_4OH, filtered to recover solids for recycle and solids washed with five 5-ml portions of ice water, does not include sulfate sulfur.

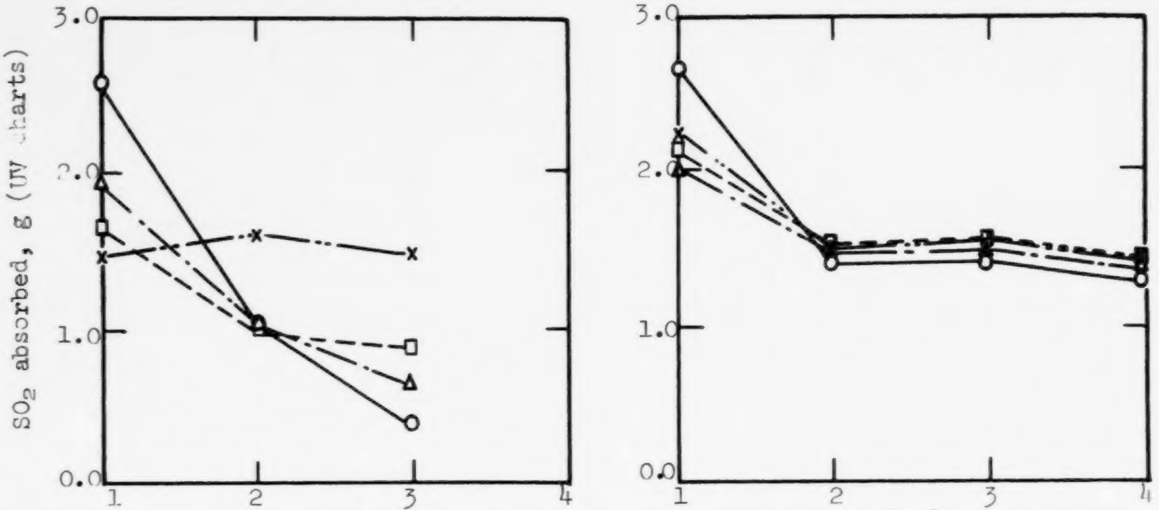
[i] 100(SO_2 absorbed - SO_2 regenerated)/SO_2 absorbed.

[j] Increased from 100 to 125 ml at beginning of third cycle to maintain fluidity during scrubbing test.

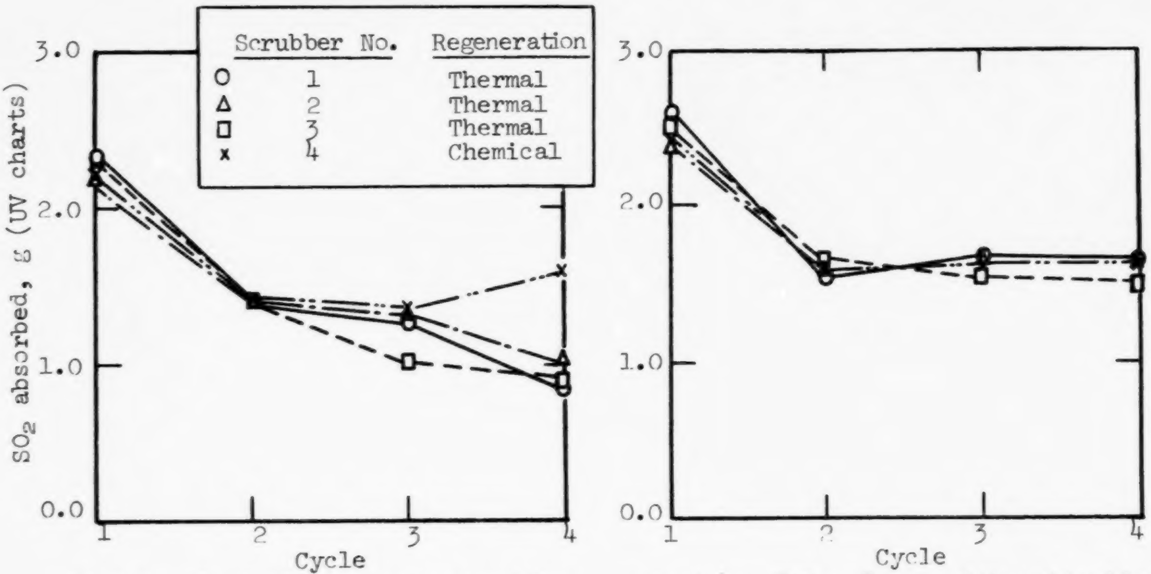
[k] Air in-leakage detected in slip-stream of gas to UV analyzer; caused operation well beyond 50% breakthrough.

[l] Filtered after standing overnight; pH was measured on filtrate.

[m] Calculated from final slurry weight less weight of wet solids from filtration.

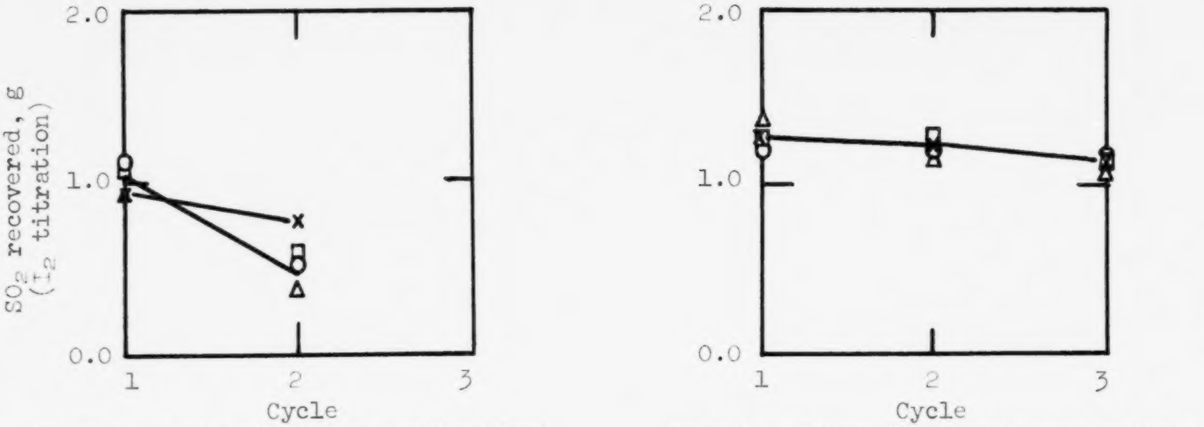


Test 1: "Dirty" gas; no antioxidant Test 2: "Dirty" gas; with antioxidant

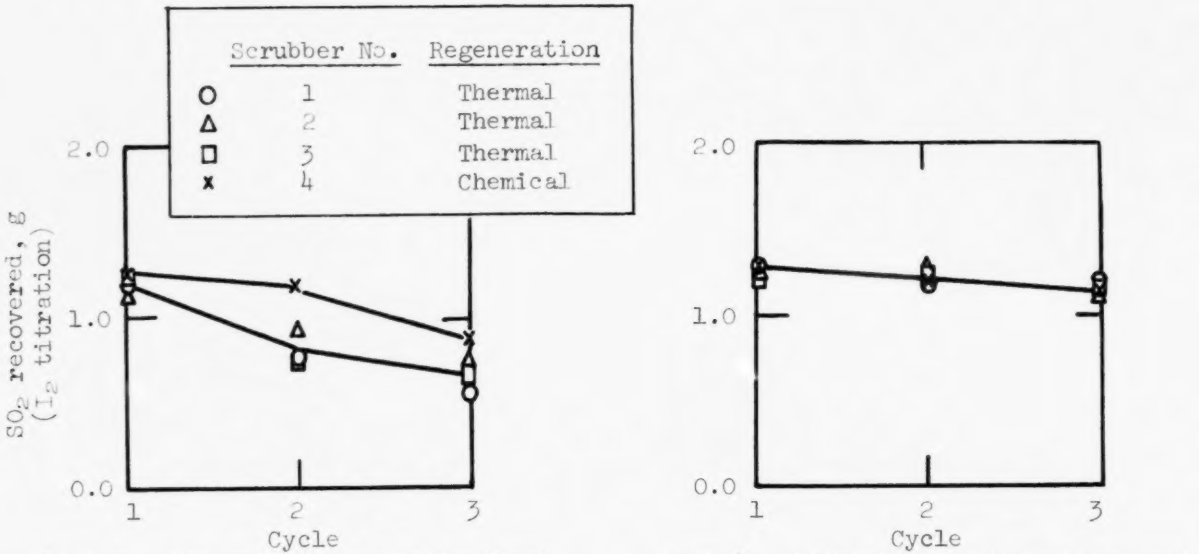


Test 3: "Clean" gas; no antioxidant Test 4: "Clean" gas with antioxidant

Figure 35. Absorption of SO$_2$ from Colbert Steam Plant gas by melamine scrubbers.



Test 1: "Dirty" gas; no antioxidant   Test 2: "Dirty" gas with antioxidant



Test 3: "Clean" gas; no antioxidant   Test 4: "Clean" gas with antioxidant

Figure 36. Recovery of SO_2 during regeneration of spent melamine scrubbers.

with the aqueous slurry, absorbed sulfur dioxide until the liquid became saturated with that component or its reacted salt. No speculation as to the identity or nature of such a component is offered.

Several trends may be seen in the data of Figure 35. First, when dirty gas was used (no prescrubber, test 1), there was a considerable spread in the absorption of SO_2 between scrubber bottles in the first cycle; this spread was not noted when clean gas (prescrubber used; test 3) was scrubbed. Next, when no antioxidant was used (test 1 and 3), the absorptive capacity of the scrubber bottles receiving thermal regenerative treatment (bottle Nos. 1, 2, and 3) declined throughout the test while the one receiving chemical regeneration (bottle No. 4) retained absorptivity longer. Third, when antioxidant (0.1% p-phenylenediamine) was present (tests 2 and 4), the absorptive capacity of the scrubbers remained about constant after the first cycle had ended and the regeneration method did not make any perceptible difference.

The amounts of SO_2 recovered during regeneration and measured by iodine titration are shown in Figure 36. The trends, discussed in the preceding paragraph, except for the spread in SO_2 absorbed during the first cycle, are reflected in the recovery data presented in Figure 36. There was a general falling off of SO_2 recovery during successive cycles when no antioxidant was added (tests 1 and 3) and, with the exception of the first cycle, slightly more SO_2 was recovered by chemical regeneration than by thermal regeneration. When antioxidant was present (tests 2 and 4), the amounts of SO_2 recovered in successive cycles were nearly constant and there was no difference between chemical and thermal regeneration. Best results were obtained when both the prescrubber and the antioxidant were used.

The spent scrubber solids were not regenerated after their last use in the scrubbers. These solids were filtered from the slurry, washed with ethanol, and dried to constant weight on a filter with dry nitrogen passing through them. Nitrogen was used to preclude oxidation. Both dry solids and the filtrates were analyzed to determine the sulfur and melamine content; the solids were analyzed also for sulfite sulfur so that the proportion oxidized could be determined. These values are given in Table 22. In all tests and in all scrubbers, the analyses of the solids indicated a fairly high degree of utilization of the melamine. The desired reaction product was $(C_3N_6H_6)_2 \cdot H_2SO_3 \cdot xH_2O$, which has an $S:C_3N_6H_6$ mole ratio of 0.5. When oxidized sulfur (sulfate) is absorbed, the reaction was considered complete when $(C_3N_6H_6)_2H_2SO_4 \cdot xH_2O$ was formed; this compound also has an $S:C_3N_6H_6$ mole ratio of 0.5. The attained $S:C_3N_6H_6$ ratios were in the range 0.48 to 0.50 except in two of the scrubbers of test 1 where the ratios were 0.43 and 0.44. These two may have been low because of the high degree of oxidation and consequent low pH in that test. As mentioned, oxidation was highest in test 1. The solids from scrubbers 1, 2, and 3, in which thermal regeneration had been used, showed 82 to 92% oxidation in test 1 (average of nearly 30%/cycle for three scrubber cycles). The solids from scrubber 4 (chemical regeneration) showed 46% oxidation; this value probably reflects insufficient regeneration of sulfate during the initial cycles since the sulfate should have been regenerated and the indicated oxidation should have resulted from the final cycle only. It is probable that more ammonium hydroxide and/or a longer regeneration period might be required when oxidation is high.

TABLE 22. CHEMICAL ANALYSES OF FINAL PRODUCTS FROM SCRUBBING STACK GAS WITH MELAMINE SLURRY

	Test 1				Test 2				Test 3				Test 4			
Prescrubber used?	No				No				Yes				Yes			
Antioxidant used?	No				Yes				No				Yes			
Scrubber bottle No.	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
Chemical analysis of solids, %																
Total S	7.4	8.3	8.3	7.6	8.6	8.6	8.5	8.2	8.0	8.3	8.3	8.0	8.2	8.4	8.5	8.0
Sulfite S	0.6	1.3	1.5	4.1	7.3	7.4	7.4	7.9	3.0	3.6	3.2	6.2	7.2	7.4	7.4	7.6
Nitrogen	45.0	44.2	44.3	45.4	45.3	45.2	44.8	43.9	43.0	44.5	44.1	43.6	45.9	45.6	45.0	43.2
S:$C_3H_6N_6$ mole ratio	0.43	0.49	0.49	0.44	0.50	0.50	0.50	0.49	0.49	0.49	0.49	0.48	0.47	0.48	0.50	0.49
Composition/100 g solids																
Moles melamine compounds	0.54	0.53	0.53	0.54	0.54	0.54	0.53	0.52	0.51	0.53	0.53	0.52	0.55	0.54	0.54	0.51
As $C_3H_6N_6$	0.07	0.01	0.01	0.07	0.00	0.00	0.00	0.01	-0.01	0.01	0.01	0.02	0.03	0.02	0.00	0.01
As $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 2H_2O$	0.02	0.04	0.05	0.13	0.23	0.23	0.23	0.25	0.09	0.11	0.10	0.19	0.23	0.23	0.23	0.24
As $(C_3H_6N_6)_2 \cdot H_2SO_4 \cdot 2H_2O$	0.21	0.22	0.21	0.11	0.04	0.04	0.03	0.01	0.17	0.15	0.16	0.06	0.03	0.03	0.03	0.01
S oxidized	91.9	84.3	81.9	46.1	15.1	14.0	12.9	3.7	64.3	56.6	61.4	22.5	12.2	11.9	12.9	5.0
Chemical analysis of filtrates, %																
Total S	0.07	0.15	0.12	0.44	0.10	0.19	0.20	0.23	0.12	0.14	0.10	0.07	0.06	0.09	0.09	0.16
Total N	0.29	0.49	0.53	0.35	0.44	0.61	0.60	0.64	0.40	0.43	0.35	0.32	0.36	0.32	0.30	0.45
NH_3-N	-	-	-	< 0.02	-	-	-	< 0.02	-	-	-	0.27	-	-	-	< 0.04
Chemical analysis of chemical regeneration liquor, %																
Cycle 1																
Total S				2.5				2.7				2.5				2.6
Total N				3.1				3.3				3.2				3.0
NH_3-N				2.1				2.4				2.3				2.5
Melamine N[a]				1.0				0.9				0.9				0.5
Cycle 2																
Total S				2.9				2.5				2.6				2.5
Total N				3.7				3.1				3.1				3.2
NH_3-N				2.6				2.5				2.3				2.3
Melamine N[a]				1.1				0.6				0.8				0.9
Cycle 3																
Total S								2.3				2.4				2.4
Total N								3.2				3.4				3.1
NH_3-N								2.3				2.4				1.9
Melamine N[a]								0.9				1.0				1.2

[a] Total N minus NH_3-N.

The high proportion of sulfur oxidized to sulfate form in test 1 was due to the lack of prescrubbing and the absence of antioxidant rather than to any unusually high oxygen content of the incoming gas. When antioxidant was added (test 2), the proportion of sulfur oxidized to sulfate form dropped to about 14% (3.5%/cycle) when thermal regeneration was used and to 3.7% when chemical regeneration was used. When oxidation was fairly low, the chemical regeneration procedure used apparently was adequate.

When a prescrubber was used without antioxidant in the scrubbers (test 3), oxidation averaged 60% (15%/cycle) when thermal regeneration was used and 22.5% when chemical regeneration was used. The relatively high value in the chemically regenerated scrubber again indicated the need for more severe conditions for chemical regeneration when oxidation is high.

Best results were obtained in test 4, in which both the prescrubber and the antioxidant were used. Oxidation averaged only 12% (about 3%/cycle) when thermal regeneration was used and 5% when chemical regeneration was used.

The filtrates from the slurries in the spent scrubbers (Table 22) contained an average of 0.15% sulfur. The nitrogen content of these solutions averaged about 0.43%, which is the equivalent of 6.5 grams melamine per liter. This dissolved melamine is returned to the scrubber in the process.

Solutions obtained from the chemical regeneration of solids from bottle No. 4 in each cycle of each test were analyzed also (Table 22). These solutions contained an average of about 0.89% nitrogen from melamine, which is equivalent to about 13.4 grams melamine per liter. This dissolved melamine would be lost from the system unless a means of recovery is devised. The regeneration solution used in the present work was quite dilute, which would increase melamine loss by solubility and would require special methods for recovery of solid ammonium sulfate. However, by recycling the regeneration solution and using anhydrous ammonia instead of ammonium hydroxide solution, the concentration of ammonium sulfate could be increased substantially and losses of melamine reduced. Also, in practice, chemical regeneration would follow thermal regeneration and involve only the amount of solids required to maintain the proportion of melamine sulfate at an acceptable level; this would obviate an otherwise necessary oxidation step for the ammonium sulfate-sulfite solution.

Conclusions

It was concluded from these tests that melamine slurry scrubbing is a chemically feasible method for removal of sulfur oxides from power plant waste gases. It was shown that the absorptive capacity of the melamine could best be maintained by the addition of an antioxidant to the system and that the antioxidant was not destroyed during regeneration (the antioxidant probably stayed in the filtrate and was not subjected to regeneration procedures). Further improvement was attained in tests in which a prescrubber also was used. The prescrubber should remove a large part of both the fly ash entrained in the gas stream and most of the sulfur trioxide present; this would lower the proportions of melamine tied up as sulfate per pass and would alleviate the problem of removing fly ash from the melamine on continued operation.

Almost complete removal of SO_2 was obtained in a single scrubber until the melamine had been about 80% exhausted; thus, a two-stage scrubber might prove sufficient in a larger scale unit. The existence of solids in the scrubber solution may preclude the use of packed scrubbers, particularly where oxidation may be fairly high. Preliminary tests had shown that, when melamine sulfate was formed in large proportions, a sticky mass plugged the gas inlet tube; this probably would foul packing.

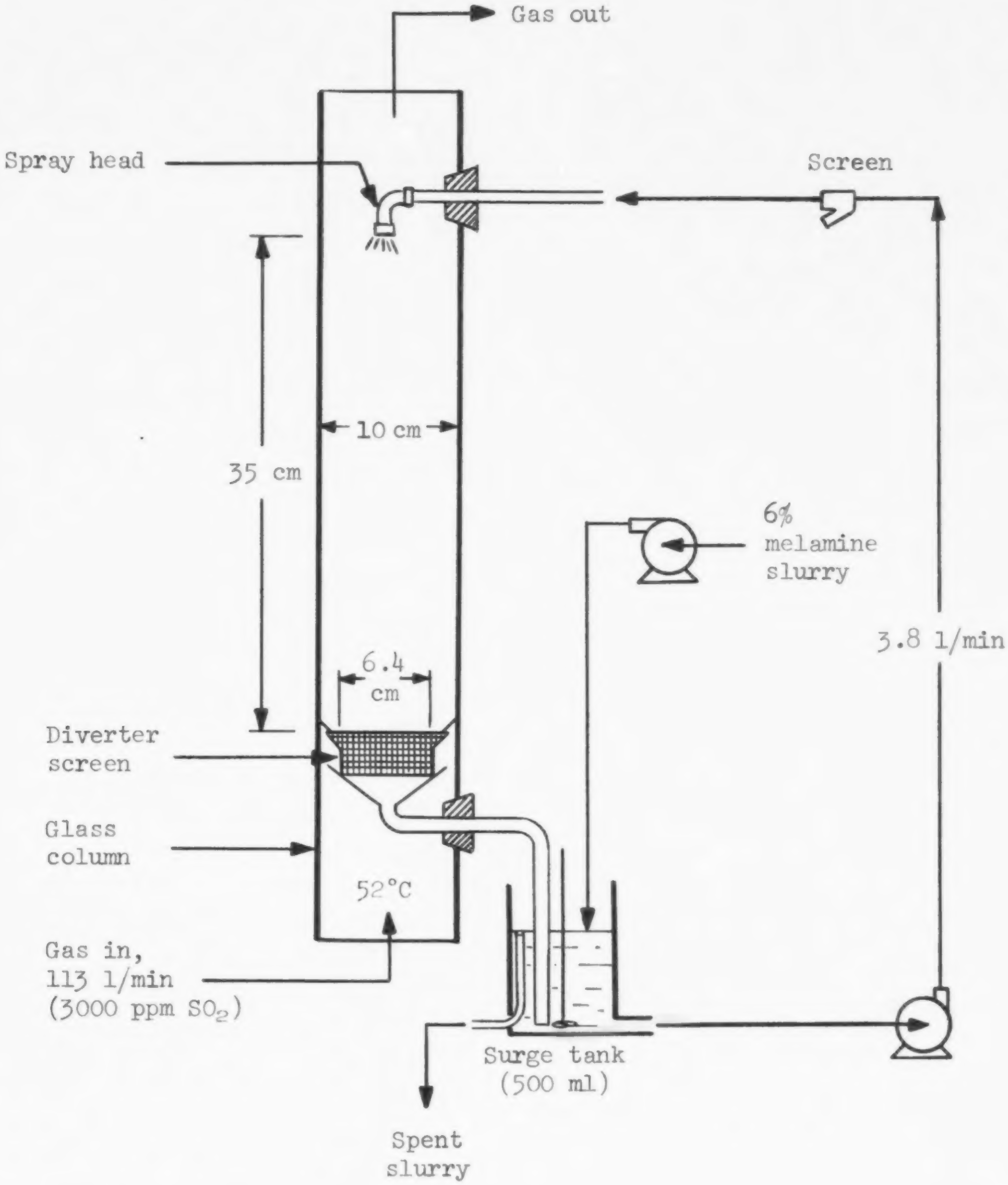
Even though a prescrubber and an antioxidant are used, a gradual increase in the proportion of melamine tied up as sulfate may be expected if thermal regeneration is used. In that case, a side-stream of spent slurry solids probably will have to be regenerated chemically.

Further testing, on a larger scale and over a greater number of cycles, will be needed to test the size of the side-stream requiring chemical regeneration and the makeup rates of melamine and antioxidant. None of the currently reported work was done to determine the most effective antioxidant or the most effective concentration.

MINIPILOT-PLANT TESTS

Previous tests of melamine slurry scrubbing for the removal of sulfur oxides from stack gases were limited to scrubbing in laboratory-type gas washing bottles. A minipilot-plant scrubber, which had been used successfully for lime and limestone slurry scrubbing, was operated in limited tests using 6% melamine ($C_3H_6N_6$) slurry as the absorbent. The gas used was produced by adding sulfur dioxide to the combustion products of natural gas to obtain a mixture containing 3000 ppm SO_2. Although testing of a variety of conditions was planned, operating problems restricted the tests; only one scrubbing stage, 100% stoichiometry, and a water prescrubber to protect the glass column from the heat of the inlet gas were tested. (A $C_3H_6N_6$:SO_2 mole ratio of 2 is considered to be 100% stoichiometry.) Because of the operational problems, the operating periods were short, liquid to gas ratios (L/G) were higher than desired, and the forward flow probably was too high at times.

The scrubber arrangement used is shown in Figure 37. The scrubber consisted of a glass tower with a full cone spray nozzle at the top, spraying downward, opposing the upward flow of stack gas which had previously been passed through a similarly constructed water prescrubber at a lower level in the tower. The slurry was removed from the tower through a centered funnel into which it was directed by a circular glass deflector and diverter screen. The slurry was drained into a 500-milliliter surge tank from which it was recirculated to the spray nozzle through a centrifugal pump, the rate being controlled by the size of the spray nozzle. Fresh slurry was added to the tank as required by a metering pump; the level in the tank was controlled by an overflow line which vented the spent slurry to a holding tank. The forward flow of slurry to the tank was about 60 milliliters per minute, so that the retention time of the slurry in the scrubber loop (scrubber + surge tank) was about 8 to 9 minutes. The recirculation rate through the spray nozzle during the more successful test periods was about 3.8 liters per minute; this resulted in an L/G of 33 liters per cubic meter and a liquid retention time of about 8 seconds in the surge tank.



Gas out
Spray head
Screen
10 cm
35 cm
6%
melamine
slurry
3.8 l/min
6.4
cm
Diverter
screen
Glass
column
52°C
Gas in,
113 l/min
(3000 ppm SO2)
Surge tank
(500 ml)
Spent
slurry

Figure 37. Spray scrubber used in melamine scrubbing tests--configuration 1.

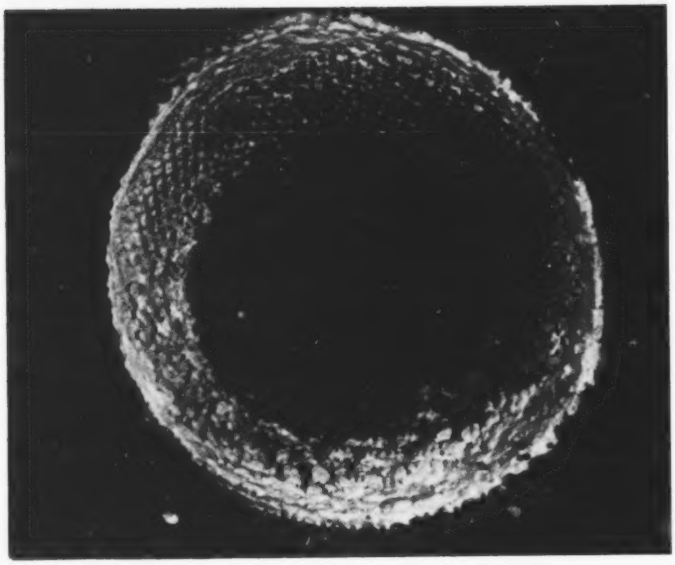
Operating problems were occasioned by the properties of the melamine and its reaction products. Although the screen analysis of the feed melamine showed > 95% minus 48 mesh, a few large particles were present that stopped up the 50-mesh strainer in the inlet line to the spray nozzles (see Figure 37). When the screen was removed, the nozzle plugged (orifice dia., approx. 1 mm, the equivalent of a 16-mesh screen). Since a larger strainer was not immediately available, the nozzle size was increased to one with an orifice about 1.5 millimeter in diameter. This nozzle also plugged. The slurry then was removed from the system and passed through a 48-mesh screen (0.297-mm opening). Oversize particles were discarded and the slurry was returned to the system. The dry melamine feed thereafter was scalped using the 48-mesh screen, and a 16-mesh strainer was installed. Little further trouble occurred due to stoppages in the slurry recirculation system.

Concurrent with the problem of strainer and nozzle stoppages, there was a buildup of solids on the diverter screen at the bottom of the tower. The slurry does not pass through this screen; the incoming gas does. The screen is present to direct the scrubbing medium into the funnel through which it exits the tower. Solids buildup was fairly rapid but, until stoppages in the feed system were eliminated, the cause could not be separated from the effects of the interrupted flow. Solids built up so rapidly on a 20-mesh diverter screen that gas flow through it became severely restricted within an hour of operation. This screen was replaced with one of 10 mesh; this plugged within about the same operating time. The solids buildup apparently began on the outside of the screens, the side through which the gas entered, and then proceeded to grow toward the slurry side. This is depicted in the photographs in Figure 38. It is assumed that the mechanics of this deposition include a dissolution of melamine in the incoming slurry, the reaction of dissolved melamine with the incoming sulfur dioxide, and subsequent rapid precipitation of melamine sulfite on the diverter screen surfaces. Petrographic analysis indicated the solids to be, primarily, melamine sulfite.

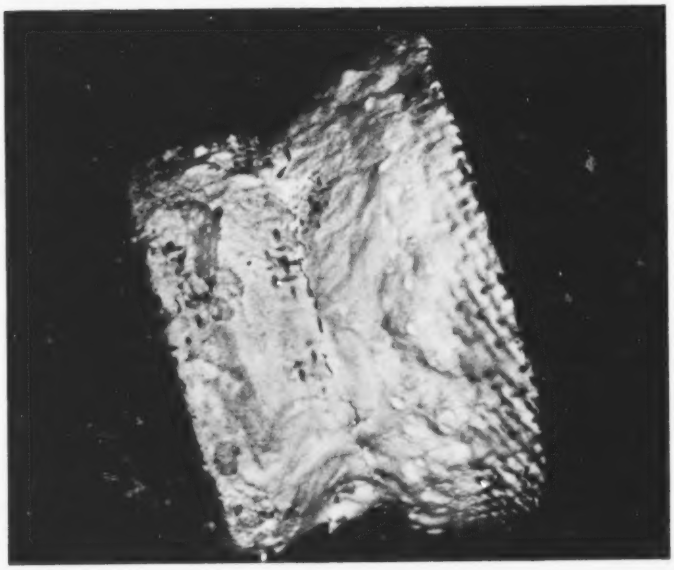
The longest period of operation in the mode indicated by Figure 37 was less than 2 hours. Throughout the sustained operating periods, however, sulfur dioxide removal was very good; better than 99% removal was attained most of the time. From these data, it appeared that melamine slurry would be a suitable absorbent in a spray scrubber provided the problem of solids buildup could be accommodated. The use of packed column-type scrubbers, however, would not seem advisable because of probable plugging problems.

One method of accommodating solids buildup would be to remove the surfaces to which the solids cling. During a period of the test, the diverter screen was removed. However, the slurry tended to flow around the edge of the stage bottom and to fall into the stage below to such an extent that continued operation was not possible.

Next, the scrubber was modified as indicated in Figure 39. The water prescrubber was removed, the diverter screen and collecting funnel were removed, and the surge tank was placed to catch the drain from the bottom of the scrubber. This configuration now resembles a wet-bottom scrubber with the gas entry at the side near the bottom. The internals at the wet-dry interface are eliminated. It is noted that, with the configuration used earlier, the



Top view



Side view (tilted)

Figure 38. Photograph of diverter screen after use in melamine scrubbing test.

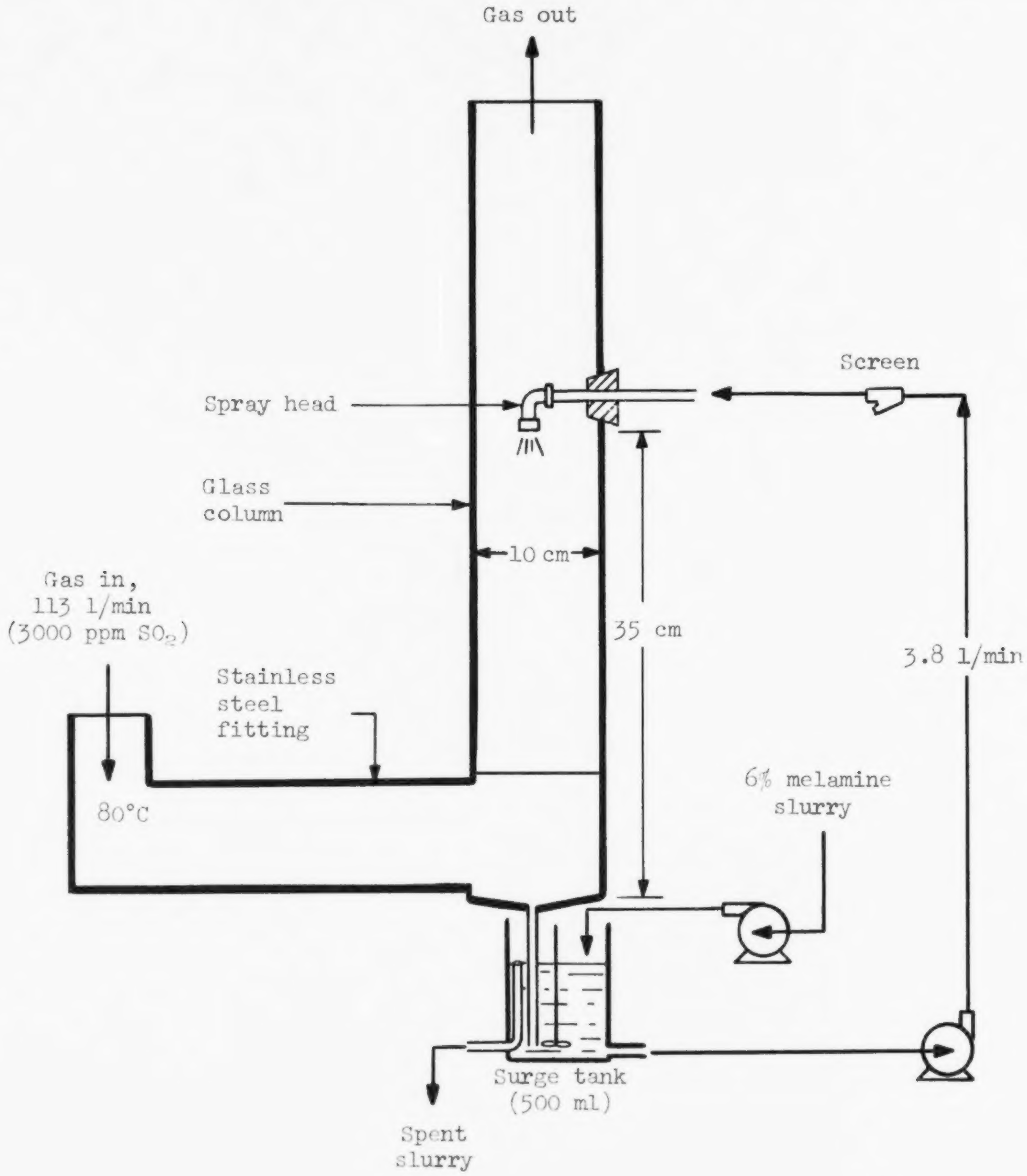

Gas out
Screen
Spray head
Glass column
10 cm
Gas in,
113 l/min
(3000 ppm SO_2)
35 cm
3.8 l/min
Stainless steel fitting
80°C
6% melamine slurry
Surge tank
(500 ml)
Spent slurry

Figure 39. Spray scrubber used in melamine scrubbing tests--configuration 2.

incoming gas leaving the prescrubber first met the slurry at the diverter screen where it made fairly good contact and then passed through the spray where it contacted the slurry again. In effect, the minipilot-plant spray scrubber stage was a double contact countercurrent scrubber. Omitting the diverter screen and funnel reduced the scrubber to one having a single contact. Omitting the prescrubber allowed the gas to contact the slurry at a higher temperature. Both these actions should be detrimental to absorption efficiency.

Operating time in the configuration described in Figure 39 was limited to 1 hour by the work schedule. Sulfur dioxide removal during that period dropped from an initial value near 100% to a final value of about 90% and the trend was still downward. Inspection of the area near the gas inlet showed little tendency to scale.

A minor problem that had been noted in the minipilot-plant run was the tendency of the melamine slurry to drain toward the inlet end of the gas duct at the bottom of the scrubber when in configuration 2. The stainless steel duct was modified as shown in Figure 40 to prevent such drainage.

A second test then was made of the single-stage, single-contact scrubber using a 6% melamine slurry containing 0.1% p-phenylenediamine as an antioxidant. The test was operated for 6 hours. Three sets of conditions were tested as shown in the following tabulation.

Test time, min	Gas flow, m^3/min	SO_2 content, ppm	Forward flow ml/min[a]	Recirculation rate, ml/min	L/G[b]	Melamine stoichiometry, %[c]	SO_2 removal, %[d]
0-180	0.113	3200	64	1068	9.5	94	75
180-235	0.113	3180	64	1347	11.9	95	78
235-300	0.113	3275	78	1347	11.9	112	80

a. 6% slurry of reagent-grade melamine in water.
b. Liters slurry per cubic meter of gas.
c. Based on equation $2C_3N_6H_6 + H_2SO_3 + 4H_2O \longrightarrow (C_3N_6H_6)_2 \cdot H_2SO_3 \cdot 4H_2O$.
d. As determined by UV analyses of inlet and outlet gases.

During the first 3 hours the melamine feed was maintained at about 1.88 moles per mole of incoming SO_2 in the stack gas (94% of stoichiometric amount of melamine). The L/G in the scrubber was 9.5 liters of slurry per cubic meter of gas. The scrubber inlet gas temperature was about 50°C, being cooled from 132°C by spraying water on the outside of the stack from the burner. At these conditions, the slurry reached about 48°C and a pH of about 4.6. Sulfur dioxide loss averaged 25%. The L/G was increased to 11.9 liters per cubic meter at 180 minutes. The pH and temperature remained about constant but the SO_2 loss decreased slightly (about 22%). An increase in forward flow at 235 minutes increased the melamine to SO_2 mole ratio to 2.25 (112% of stoichiometric). This decreased the slurry temperature slightly (about 2°C) and further decreased loss of SO_2 to about 20%. Inspection after the test showed little buildup at the bottom of the scrubber. There was some buildup on the scrubber walls above the spray head where melamine spattered or was carried

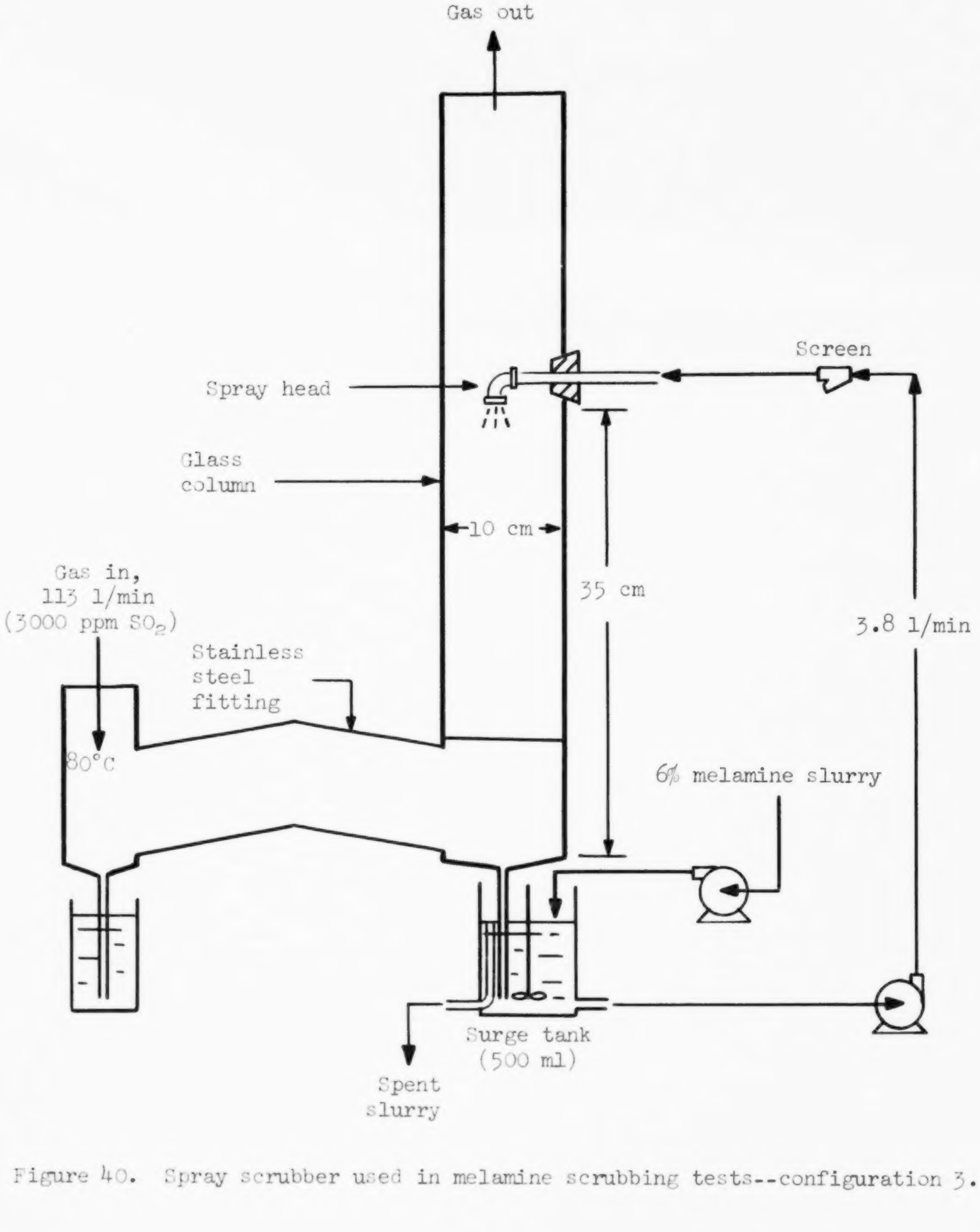

Gas out
Screen
Spray head
Glass column
10 cm
35 cm
Gas in,
113 l/min
(3000 ppm SO_2)
3.8 l/min
Stainless steel fitting
80°C
6% melamine slurry
Surge tank
(500 ml)
Spent slurry

Figure 40. Spray scrubber used in melamine scrubbing tests--configuration 3.

up as a mist. The material in this buildup was almost entirely a weak, pasty cementation of melamine sulfite $[(C_3N_6H_6)_2 \cdot H_2SO_3 \cdot 4H_2O]$ that was easily removed with a low velocity stream of water or by scraping. It should be easy to remove such material from a mist eliminator with makeup water.

Sulfur dioxide removal was such that acceptable removal would have been possible with two such stages in series or with a crossflow scrubber.

Conclusions

It was concluded that melamine scrubbing could be used to remove SO_2 from waste gas streams but that packed scrubbers would probably cause trouble with plugging. If spray scrubbers are used, two such scrubbers probably will be required; a crossflow type might be suitable. The inclusion of an antioxidant is suggested to limit oxidation as much as possible.

When using actual stack gas, the use of a prescrubber to cool the gas, remove most of the SO_3 present, and remove most of the fly ash is suggested. The cooler gas will react more completely with melamine; melamine sulfite exhibits a vapor pressure (SO_2) at moderate temperatures. The removal or limiting of SO_3 is important because melamine sulfate is not regenerated thermally. Limiting fly ash will make processing the melamine easier and probably will help to limit oxidation; the removal of fly ash from the melamine, when it becomes necessary, will be expensive.

SODIUM SULFITE-MELAMINE PROCESS

PRODUCTION OF MELAMINE SULFITE FROM SODIUM BISULFITE SOLUTION AND MELAMINE

A cyclic process has been proposed (13) for the removal and recovery of sulfur dioxide from waste stack gas in which the gas would be scrubbed with a sodium sulfite (Na_2SO_3) solution to produce sodium bisulfite ($NaHSO_3$) solution, leaving a waste gas essentially free of SO_2 to be expelled into the atmosphere. As a second step, the $NaHSO_3$ solution would be reacted with melamine ($C_3H_6N_6$) to regenerate the Na_2SO_3 solution and precipitate melamine sulfite $[(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot xH_2O]$. Next, the melamine sulfite would be regenerated thermally or chemically to recover $C_3H_6N_6$ for recycle and SO_2 in useful form. Laboratory-scale tests now have been made with reagent-grade chemicals to determine the feasibility of the $C_3H_6N_6$-$NaHSO_3$ reaction step as shown in the following equation:

$$2NaHSO_3 + 2C_3H_6N_6 \longrightarrow Na_2SO_3 + (C_3H_6N_6)_2 \cdot H_2SO_3 \cdot xH_2O$$

In the present work, the variables studied were the $C_3H_6N_6$:$NaHSO_3$ mole ratio, temperature, sodium bisulfite concentration, and test time. Test procedure was as follows: The required amounts of $NaHSO_3$ and water for each test were combined and placed in a water bath of controlled temperature. This solution was given time to equilibrate while being stirred. When test temperature had been reached, the $C_3H_6N_6$ was added as a finely divided powder (96% -48 mesh) to the $NaHSO_3$ solution and stirred for the required test period. The final slurry was filtered through glass fiber filter paper on a medium-frit funnel. The cake was slurried twice with water of weight approximately 1-1/2 to 2 times the weight of $C_3H_6N_6$ used, and was refiltered. The cake then was washed twice with ethanol and allowed to dry at room temperature under house vacuum. After drying, the solids were submitted for analysis to determine the percent sodium, nitrogen, total sulfur, and SO_2-sulfur (sulfite sulfur). The solids were also examined microscopically for identification of the crystal phases present and for comparative particle size of the melamine sulfite crystals. Collected data and some calculations from these data are shown in Table 23. The $NaHSO_3$ used for these studies also was analyzed; this analysis along with the percent of the $NaHSO_3$ oxidized, as calculated from this analysis, is given as a footnote to Table 23.

The sodium analysis of the product solids indicates the efficiency of the washing procedure. The only test which indicates the need for more thorough washing is test 3 in which the more concentrated $NaHSO_3$ solution (25%) was used. This also is the only test in which the amount of sulfur associated with the sodium is large enough to affect the total sulfur analysis significantly. Since, as indicated later, the melamine apparently exhibited a preferential reaction with sulfite, the sodium probably would be present as

TABLE 23. PRODUCTION OF MELAMINE SULFITE FROM MELAMINE AND SODIUM BISULFITE SOLUTION (LABORATORY TEST DATA)

Test No.	2B	3	4	5	6	7	8	9	10
$C_3H_6N_6$:$NaHSO_3$[a] mole ratio	0.8	0.8	0.8	1.0	0.8	0.6	0.6	0.8	0.8
$NaHSO_3$ concentration in solution, %	15	25	15	15	15	15	15	15	15
Test time, min	60	60	60	30	30	60	60	60	60
Temperature, ° C	52	52	38	52	52	52	38	27	16
Input formulation, g									
$NaHSO_3$	10.41	10.41	10.41	10.41	10.41	10.41	10.41	10.41	10.41
Melamine	10.9	10.09	10.09	12.61	10.09	7.57	7.57	10.90	10.90
H_2O	58.97	31.22	58.97	58.97	58.97	58.97	58.97	58.97	58.97
Cake weight, g	13.45	18.6	15.0	16.15	13.4	9.93	10.94	15.36	15.31
Chemical analysis of solids, %									
Na	0.04	0.58	0.05	0.06	0.04	0.05	0.02	0.01	0.01
Total S	5.7	5.7[b]	7.1	5.1	6.4	6.5	7.3	7.2	7.5
SO_2-S	5.3	5.0	6.3	4.7	6.0	6.5	7.3	7.1	7.3
N	51.6	37.7	43.8	50.7	48.7	47.8	44.0	45.6	45.5
Calculated indices									
Sulfur oxidized, % of total	7.01	12.3[b]	11.3	7.8	6.3	0	0	1.4	2.7
S:$C_3H_6N_6$ mole ratio	0.29	0.40[b]	0.43	0.26	0.34	0.36	0.44	0.41	0.43
Residual melamine, % of input	42.03	20.63[b]	13.79	47.92	31.97	28.57	13.04	18.03	14.16
Bisulfite reacted, % of input	46.40	64.00	68.80	52.00	54.40	43.22	52.82	65.60	68.80
Particle size									
Av. microns	11 x 35	37 x 63	43 x 148	24 x 59	17 x 36	8 x 21	40 x 108	31 x 85	43 x 69
Av. area compared with test 4, %	6	37	100	22	10	3	68	41	47

[a] Chemical analysis of $NaHSO_3$:

%			Calculated
Na	Total S	SO_2-S	% oxidized
26.9	31.5	29.8	5.4

[b] Corrected value for sulfur not combined with sodium.

sodium sulfate. Therefore, calculations were made to correct the total and sulfate sulfur analysis by excluding that tied up with the sodium. The corrected values are given in the tables.

Evaluation was made of the measured responses and calculations from those responses. Calculations include: percent of total sulfur oxidized; $S:C_3H_6N_6$ mole ratio in the product; percent residual melamine; percent bisulfite reacted; and average particle size of the melamine sulfite crystals in the solid product. Oxidation to the sulfate form is undesirable since melamine sulfate does not regenerate thermally to $C_3H_6N_6$, and chemical regeneration would be required to recover that portion of the $C_3H_6N_6$. The $S:C_3H_6N_6$ ratio indicates the degree of reaction. In the reaction of $NaHSO_3$ solution with $C_3H_6N_6$, it is advantageous to react as much of the sulfite as possible; use of an excess of $C_3H_6N_6$ (low $S:C_3H_6N_6$) would encourage high degree of reaction. However, in the thermal regeneration step it is desirable to have as high an $S:C_3H_6N_6$ ratio as possible in order to reduce the energy requirement. An optimization of this ratio will be a major consideration in the design of the system. The nitrogen analysis offers a means of measuring the $C_3H_6N_6$ content of the product (including that present as melamine sulfite and sulfate). The percent residual melamine and percent bisulfite reacted are measures of the degree of completion of the desired reaction. Particle size of the product affects filtration rates; therefore, larger particles are desirable. The effect of the four variables on these responses is shown in Table 24. The values footnoted b are so small as to be equal to or less than the precision of the analyses and therefore probably are not significant. Those values footnoted c lie within twice the value of the accuracy of the analyses and are therefore of questionable significance.

Effect of Sodium Bisulfite Concentration

The effect of $NaHSO_3$ concentration on the responses measured and calculated is given in the first column of Table 24. With increase in concentration from 15 to 25%, the melamine sulfite crystal size increased by 84%, but 43% more of the total sulfur underwent undesirable oxidation to sulfate, while SO_2-sulfur decreased, nitrogen decreased, and the percent residual melamine decreased by 51%. The $S:C_3H_6N_6$ mole ratio indicated more complete reaction ($S:C_3H_6N_6$ = 0.40, 27% greater) with the higher concentration (desired $S:C_3H_6N_6$ mole ratio is 0.5). Percent of bisulfite reacted increased from 46 to 64% (Table 23).

Effect of Temperature

A maximum temperature of 52°C was selected for testing since aqueous media scrubbers on coal-fired boiler stack gas will equilibrate at about that temperature. It should be possible to cool the reaction to 38°C using river water as the coolant, so tests were made at this temperature, also. A comparison of the results at 52°C and 38°C revealed such great differences, with the values moving in the desirable direction at the lower temperature, that tests were made also at 27°C and 16°C.

TABLE 24. EFFECT OF VARIABLES--DIFFERENCES IN RESPONSES DUE TO VARIABLES

Variable	$NaHSO_3$ concentration, %	Temperature, °C							$C_3H_6N_6$:$NaHSO_3$ mole ratio			Time, min
	15 25	52 38	52 27	52 16	38 27	38 16	27 16	52 38	0.8 0.6	0.8 0.6	1.0 0.8	60 30
Test No.	2B 3	2B 4	2B 9	2B 10	4 9	4 10	9 10	7 8	2B 7	4 8	5 6	2B 6
Analysis, %												
Na	+0.54(93)[a]	+0.01(20)[b]	-0.03(75)	-0.03(75)	-0.04(80)	-0.04(80)	0	-0.03(60)	+0.01[b](20)	-0.03 (60)	-0.02[c](33)	0
Total S	0	+1.4 (20)	+1.5 (21)	+1.8 (24)	+0.1 (1)[b]	+0.4 (5)	+0.3 (4)	+0.8 (11)	+0.8 (12)	+0.2[c] (3)	+1.3 (20)	+0.7 (11)
SO_2-S	-0.3 (6)	+1.0 (16)	+1.8 (25)	+2.0 (27)	+0.8 (11)	+1.0 (14)	+0.2 (3)[c]	+0.8 (11)	+1.2 (18)	+1.0 (14)	+1.3 (22)	+0.7 (12)
N	-13.9 (27)	-7.8 (15)	-6.0 (12)	-6.1 (12)	+1.8 (4)	+1.7 (4)	-0.1(0.2)[b]	-3.8 (8)	-3.8 (7)	+0.2[c](0.5)	-2.0 (4)	-2.9 (6)
Melamine sulfite comparative particle size[d]	+31 (84)	+94 (94)	+37 (90)	+41 (87)	-59 (59)	-53 (53)	+6 (13)	+65 (96)	-3 (50)	-32 (32)	-12 (55)	+4 (40)
Calculated indices												
S oxidized, %	+5.29(43)	+4.29(38)	-5.61(80)	-4.31(62)	-9.9 (88)	-8.6 (76)	+1.3 (48)	0	-7.01(100)	-11.3 (100)	-1.5 (19)	-0.71(10)
S:$C_3H_6N_6$ mole ratio	+0.11(27)	+0.14(33)	+0.12(29)	+0.14(33)	-0.02 (5)[b]	0	+0.02 (5)[c]	+0.08(18)	+0.07 (19)	+0.01[b] (2)	+0.08 (24)	+0.05(15)
Residual melamine, % of input	-21.40(51)	-28.24(67)	-24.00(57)	-27.87(66)	+4.24(24)	+0.37 (3)	-3.87(21)[c]	-15.53(54)	-13.46 (32)	-0.75[b] (5)	-15.95 (33)	-10.0 (24)
Bisulfite reacted, % of input	+17.6 (28)	+22.4 (33)	+19.2 (29)	+22.4 (33)	-3.2 (5)	0 (0)	+3.2 (5)	+9.6 (18)	-3.18 (7)	-15.98 (23)	+2.4 (4)	-8 (15)
Other conditions												
$C_3H_6N_6$:$NaHSO_3$ mole ratio	0.8	← 0.8 →						0.6	-	-	-	0.8
Temperature, °C	52	-						-	52	38	52	52
Time, min	60	60						60	60	60	30	-
$NaHSO_4$ concentration, %	-	15						15	15	15	15	15

---

[a] Numbers in parentheses represent % difference in the two tests.
[b] Insignificant.
[c] Significance questionable.
[d] Average crystal size area in each test compared with average crystal size area in test 4 using 100% for test 4.

Effects of temperature are most easily seen in Figure 41. The proportion of sodium in the cake decreased as temperature decreased, which indicated either better washing or better exclusion of the liquid phase from the crystals. As the temperature decreased, total and sulfite sulfur contents increased and the nitrogen content decreased; these changes, reflected in higher $S:C_3H_6N_6$ ratio, indicated a more complete reaction at the lower temperature. Percent of bisulfite reacted at 38°C was 69% versus 46% at 52°C (Table 23). At 27°C and 16°C, the percent reaction was 66 and 69%, respectively. More complete reaction is indicated also in the curve showing residual melamine (calculated as % of $C_3H_6N_6$ above a $C_3H_6N_6:S$ mole ratio of 2). The particle size of the melamine sulfite crystals, indicated by the average area of one face of the crystals as viewed under the microscope (random orientation), increased drastically as the temperature decreased from 52°C to 38°C but then decreased as temperature was lowered to 27°C and 16°C. Petrographic examination showed the products at 38°C and lower to be a single phase, probably $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O$, while the product at 52°C was a mixture of at least three different salts. The proportion of sulfur oxidized, when the $C_3H_6N_6:NaHSO_3$ input mole ratio was 0.8, tended to follow the pattern exhibited by particle size; maximum oxidation occurred at 38°C. It is noted that, when the $C_3H_6N_6:NaHSO_3$ input mole ratio was 0.6 (tests 7 and 8), the oxidation value was 0; this may indicate a preferential reaction of melamine with sulfite.

Effect of Melamine to Sodium Bisulfite Mole Ratio

This effect is best seen in Figure 42. Sodium content of the filter cake was little affected but tended to trend downward as the ratio was decreased from 1.0 to 0.8 to 0.6 mole $C_3H_6N_6$ per mole $NaHSO_3$. As expected, total and sulfite sulfur in the filter cakes increased and nitrogen decreased as the ratio decreased. The $S:C_3H_6N_6$ mole ratios in the products reflected chiefly those in the raw materials; residual melamine decreased as the proportion of melamine in the raw materials decreased. Response of percent bisulfite reacted was greatest in the tests at 38°C (tests 4 and 8); there was a 23% decrease in percent reacted (53 vs. 69% reacted) as a result of lowering $C_3H_6N_6:NaHSO_3$ mole ratio from 0.8 to 0.6. The most meaningful responses were in particle size which tended to decrease with decrease in the input ratio, and in the proportion of sulfur oxidized which also decreased with decrease in the input ratio.

Effect of Time

This effect is shown in the last two columns of Table 24. The direction of all the responses, excepting possibly oxidation, is the reverse of that expected. Most of the differences in response were fairly small, however. Further testing of this variable will be required to clarify the results.

Petrographic Analyses

From petrographic analyses, at least four different phases were found in the product solids. As many as three of these phases were found to exist simultaneously in the product from some of these studies. In the products with the largest melamine sulfite crystals (tests 4 and 8) only one phase was

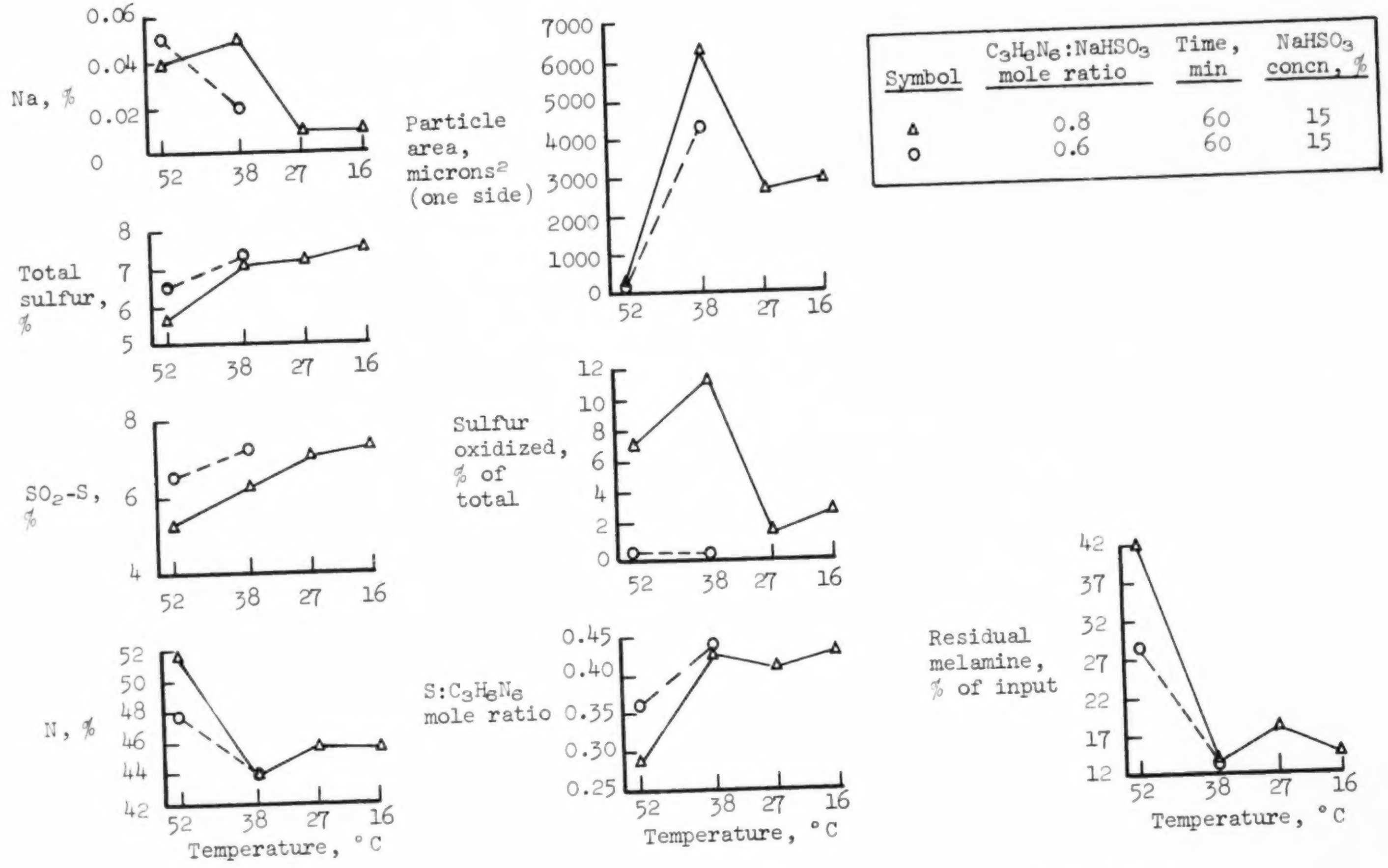


Figure 41. Effect of reaction temperature on composition of filter cake from reaction of melamine with sodium bisulfite solution.

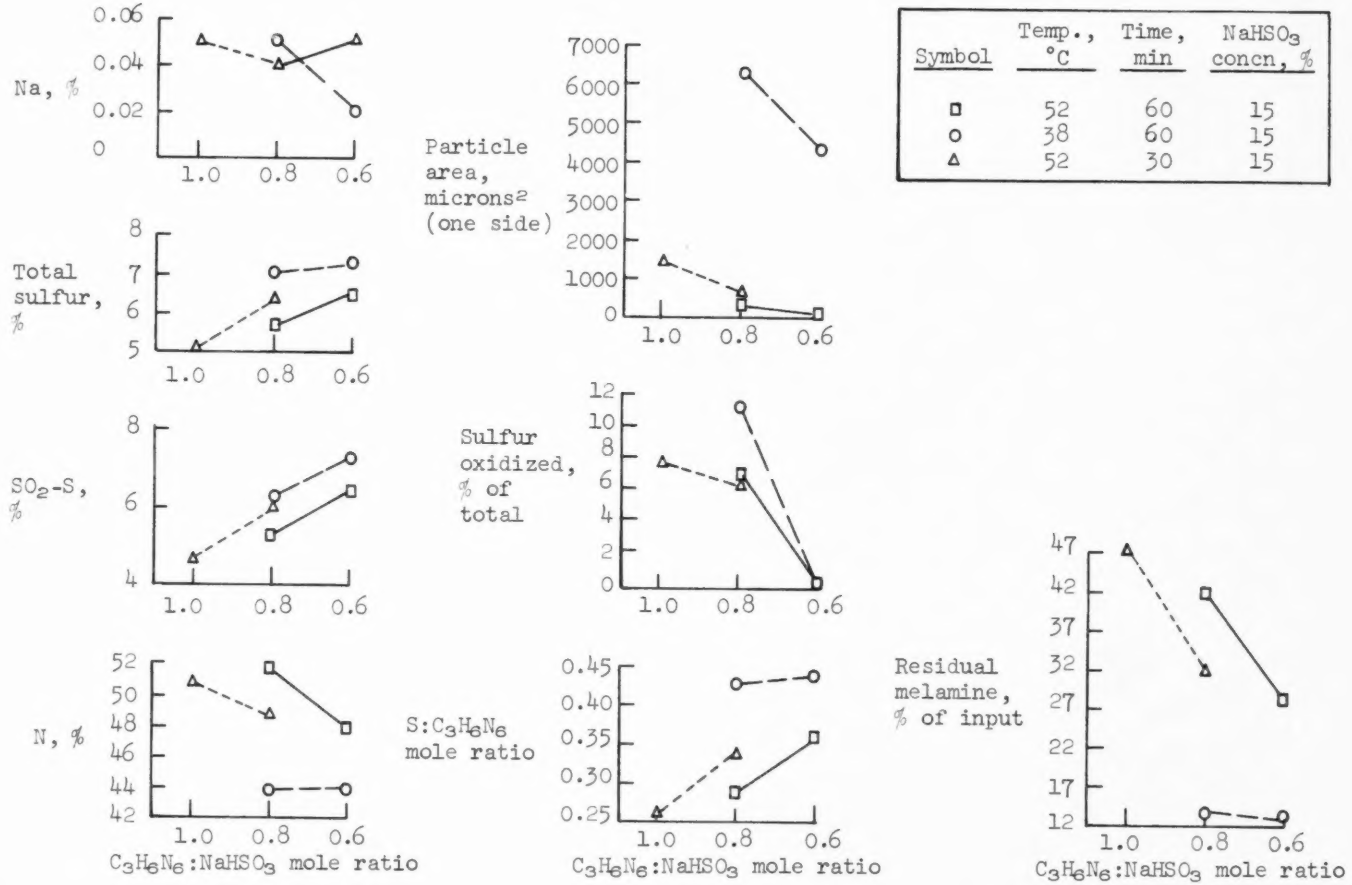


Figure 42. Effect of $C_3H_6N_6$:$NaHSO_3$ mole ratio on composition of filter cake from reaction of melamine with sodium bisulfite solution.

found and this phase, later identified as melamine sulfite tetrahydrate $[(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O]$, was different from those in the products containing three phases. The surfaces of the crystals were pitted as a result of deterioration.

Because of the deterioration of the crystals, there was a question concerning a possible change in crystal phase as a result of drying the product solids. Therefore, repetitions of tests 4 and 7 were made excluding the drying procedure. One repetition of test 4 (4-V-1) and two repetitions of test 7 (7-V-1 and 7-V-1A) were made. Data from these tests are shown in Table 25. In test 7-V-1 there was difficulty maintaining a constant temperature of 52°C. The temperature tended to rise. Temperature was stable in tests 4-V-1 and 7-V-1A. Petrographic analysis of the product solids was made immediately following the tests and again 16 hours later. During this 16-hour interval the crystals remained in the mother liquor at room temperature.

Petrographic analysis revealed that immediately following the tests, the melamine sulfite crystals in tests 4-V-1 and 7-V-1A were of the same phase while the melamine sulfite crystals in test 7-V-1 were of a different phase and much smaller than those from the other two tests. The melamine sulfite phase existing in tests 4-V-1 and 7-V-1A was the same as that in tests 4 and 8 and was identified as melamine sulfite tetrahydrate $[(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O]$. After 16 hours, the crystals in test 7-V-1 had grown to be significantly larger than the crystals of tests 4-V-1 and 7-V-1A and were now the same phase as in those tests. None of the original phase existed in test 7-V-1 after 16 hours.

Thermal Analysis

Analysis then was made of the melamine sulfite tetrahydrate by differential scanning calorimetry at 20°C per minute. Three peaks were shown (Figure 43) upon heating from 27°C to 150°C. The first peak reached a maximum at 84°C, the second at 94°C, and the third at 119°C. In further tests at 5°C per minute, these peaks were separated. The weight loss represented by the first peak was 9% of the original weight of the sample which is equivalent to 2 moles of water. The weight loss depicted by the second peak is equivalent to 1 mole of water, and the weight loss after completion of the third peak is equivalent to an additional mole of water plus 1 mole of H_2SO_3. This analysis then supports the microscopic analysis, indicating that the melamine sulfite analyzed exists as the tetrahydrate. It also offers a possible method of separation of a major portion of the water from the SO_2 on thermal decomposition. The indication is that controlled heating could be used to dehydrate melamine sulfite tetrahydrate prior to further thermal treatment for regeneration.

Conclusions

It appears that the degree of completion of the reaction (indicated by the $S:C_3H_6N_6$ ratio, % residual melamine, and % bisulfite reacted) may be controlled by adjustment of the $C_3H_6N_6:NaHSO_3$ ratio and the temperature of the reaction. In these tests 87% utilization of melamine (test 8) and 69% reaction of bisulfite (tests 4 and 10) were the best obtained. The degree of

TABLE 25. PRODUCTION OF MELAMINE SULFITE FROM MELAMINE AND SODIUM BISULFITE SOLUTION--ANALYSIS OF PRODUCTS

Test No.	4-V-1	7-V-1	7-V-1A
$C_3H_6N_6$:$NaHSO_3$ mole ratio	0.8	0.6	0.6
$NaHSO_3$ concentration in solution, %	15	15	15
Test time, min	60	60	60
Temperature, °C	38	52[a]	52
Input formulation, g			
$NaHSO_3$	10.41	10.41	10.41
Melamine	10.09	7.57	7.57
H_2O	58.97	58.97	58.97
Particle size (av.), microns			
Immediate	40 x 40 x 120	1 x 25 x 25	100 x 100 x 150
16 hours	40 x 40 x 120	150 x 300 x 600	100 x 100 x 150
Indices of refraction			
Immediate			
α	1.478	1.470	1.478
β	1.703	1.720	1.703
γ	1.721	1.764	1.721
16 hours			
α	1.478	1.478	1.478
β	1.703	1.703	1.703
γ	1.721	1.721	1.721

[a] Difficulty in holding temperature, fluctuation upward.

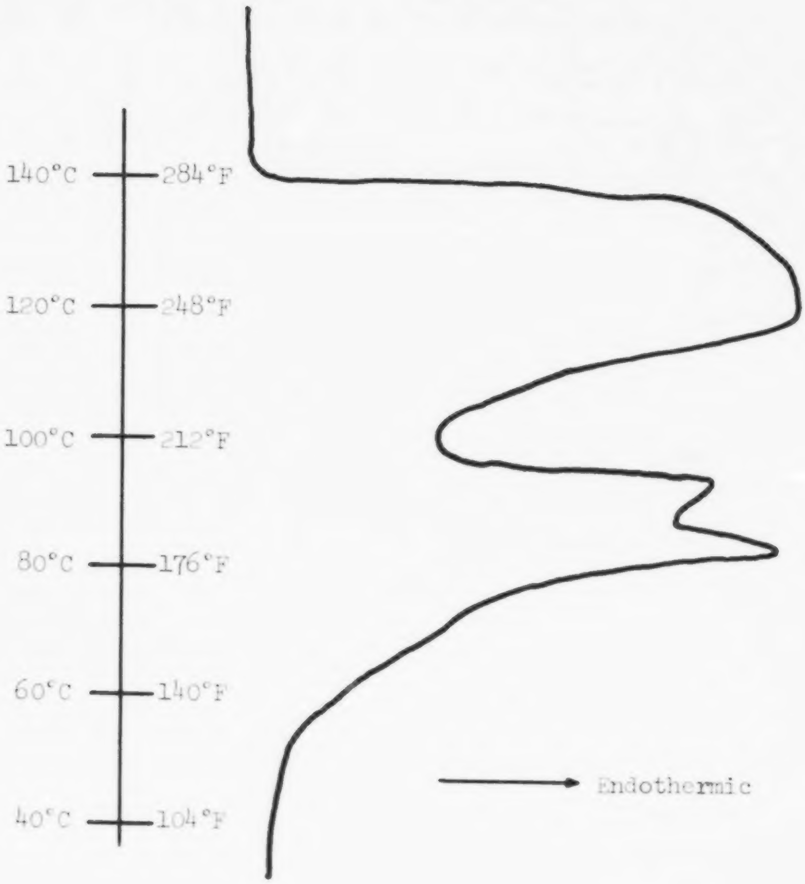


Figure 43. DSC trace of melamine sulfite tetrahydrate.

hydration may be controlled by the temperature of the reaction, also. Control of the type and size of the reaction product should be possible. The degree of oxidation encountered probably will not be harmful to the $C_3H_6N_6$-$NaHSO_3$ reaction, but can be a problem in filtration and thermal regeneration. The work performed lends credence to the feasibility of the proposed process.

PRODUCTION AND CHARACTERIZATION OF MELAMINE-SULFUR OXIDE ADDUCTS IN PURE FORM

Further studies were made to produce, in relatively pure form, the four products of the reaction of melamine with sodium bisulfite found in the earlier tests and to characterize them. All four were produced, but only three of these in homogeneous products. The optical descriptions of these four materials and their empirical formulas (calculated from chemical analyses) are given in Table 26.

Test Plan

All test products were made in a 15% sodium bisulfite solution with a melamine to sodium bisulfite mole ratio of 0.6, and all slurries were stirred continuously during the test period. Test time and temperature varied (Table 27). Test solutions 3-1 and 3-2 contained 0.05% p-phenylenediamine, an antioxidant; the other test solutions contained no antioxidant. Heated test products remained in the mother liquor while cooling slowly to ambient temperature to allow maximum crystal growth. The solids were then filtered, washed, dried, and submitted to the petrographic lab for analysis. Products were analyzed chemically for percent total sulfur, SO_2-sulfur, and nitrogen. Differential scanning calorimetry (Perkin-Elmer Differential Scanning Calorimeter, Model DSC-1) tests were made on each product, using about 10-milligram samples. Test time and temperature, chemical analyses, calculations from those analyses, and calculated weight loss during differential scanning calorimetry (DSC) testing are given in Table 27 along with refractive indices.

Test Results

The monoclinic prism produced in test 2-1 was identified as melamine sulfite tetrahydrate, $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O$, with 14% oxidation. This compound was produced in several tests with varying degrees of oxidation and can be identified petrographically, although the percent oxidation cannot be determined petrographically. When this salt is produced in a sodium bisulfite solution with melamine added to the solution, it is several hours before all the melamine reacts. The melamine reacts more quickly when the slurry is heated, but at temperatures above 40°C salts other than the tetrahydrate are formed, largely the dihydrate. When the dihydrate is allowed to remain in the mother liquor at temperatures below 25°C for several hours, the tetrahydrate begins to form. On exposure to air the tetrahydrate crystals deteriorate; acetone also erodes these crystals. The weight loss on heating in the DSC was 36.8%; calculated H_2SO_3 + H_2O content amounted to 36.7%. It appears that all of these components are lost on heating to 187°C.

TABLE 26. OPTICAL DESCRIPTION OF ADDUCTS

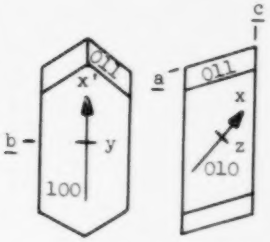
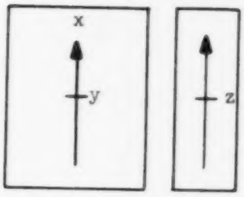
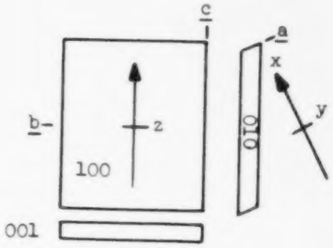
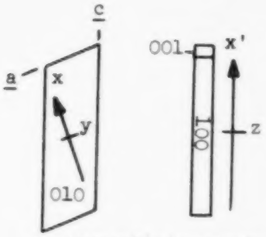
Common habit	Test No. and crystal description
 c 011 x' a 011 x b y z 100 010 Monoclinic prism	Test 2-1 These crystals precipitate as monoclinic, 2/m prisms elongated along c, modified by the (010) and (100) and terminated by {011}. b = y n α 1.478, n β 1.703, n γ 1.721 Probable formula: $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O$
 Orthorhombic tablet	Test 2-2 This salt crystallizes as orthorhombic tablets, tabular on the x-y plane and slightly elongated along x. n α 1.450, n β 1.721, n γ 1.735 Probable formula: $(C_3H_6N_6)_3 \cdot H_2SO_4 \cdot 4H_2O$
 Monoclinic plate	Test 2-5 These crystals precipitate as monoclinic, 2/m plates elongated along c, modified by (010) and (001). b = z n α 1.473, n β 1.747, n γ 1.764 Probable formula: $(C_3H_6N_6)_2 \cdot H_2SO_4 \cdot 2H_2O$
 Monoclinic blade	Test 3-1 This salt crystallizes as monoclinic, 2/m (010) blades elongated along c modified by small (001) and (100). This salt also exists as elongated plates and rods. b = z n α 1.478, n β 1.746, n γ 1.774 Probable formula: $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 2H_2O$

TABLE 27. SODIUM SULFITE-MELAMINE PROCESS--PREPARATION OF PURE REACTION PRODUCTS FOR CHARACTERIZATION

Test No.	2-1	2-2	2-3	2-5		3-1	3-2	
$C_3H_6N_6$:S mole ratio in mixture	0.6	0.6	0.6	0.6		0.6[a]	0.6[a]	
Test time, hr								
Before heating	0	18	18	72		0	72	
Heating	0	6	6	1		5	1.75	
Stored at room temperature	21	0	23	134		16	21	
Temperature to which heated, °C	Ambient	70	> 70	88		70	88	
Crystal habit of solids[b]	MPR	OTB	MBL	MBL[c]	MPL[d]	MBL	MBL[e]	MRD[f]
Refractive indices								
α	1.478	1.450	1.460	1.471	1.473	1.478	1.472	1.475
β	1.703	1.721	1.735	1.742	1.747	1.746	1.738	1.740
γ	1.721	1.735	1.768	1.765	1.764	1.774	1.768	1.772
Chemical analysis, %								
Total S	7.66	5.4	8.9	8.6		8.4	8.5	
SO_2-S	6.61	0.3	3.1	5.35		7.1	7.1	
Nitrogen	40.10	46.2	42.2	43.6		44.6	45.0	
Calculated indices								
S oxidized, % of total	13.71	94.44	65.17	37.79		15.48	16.47	
$C_3H_6N_6$:S mole ratio	2.00	3.25	1.81	1.93		2.02	2.02	
H_2O:S[g] mole ratio	4.57	4.71	2.20	2.26		2.31	2.10	
Weight loss on heating, %[h]	36.7	15.1	19.0	24.6		29.1	28.2	
DSC test weight loss, %[i]	36.8	13.8	15.6	23.8		29.1	30.2	

[a] 0.05% p-phenylenediamine added as antioxidant.

[b] MPR = monoclinic prism, OTB = orthorhombic tablet, MPL = monoclinic plate, MBL = monoclinic blade, MRD = monoclinic rod.

[c] 60% of solids.

[d] 20% of solids.

[e] 50% of solids.

[f] 35% of solids.

[g] Calculated as $\left[\frac{100 - \text{wt. } C_3H_6N_6 - \text{wt. } H_2SO_4 - \text{wt. } H_2SO_3}{18}\right] \div \left[\frac{\%\ S}{32}\right] = H_2O\text{:S mole ratio.}$

[h] Loss of $H_2O + H_2SO_3$. No loss of H_2SO_4 or $C_3H_6N_6$.

[i] Differential scanning calorimeter tests heating 10-mg samples to 187° or 227°C at 20°C/min.

The orthorhombic tablets produced in test 2-2 were 94% sulfate. These crystals are eroded by acetone but do not deteriorate on air drying. Chemical analysis indicates this compound has 3 moles of melamine to 1 mole of sulfur with approximately four waters of hydration $[(C_3H_6N_6)_3 \cdot H_2SO_4 \cdot 4H_2O]$. Calculations from the chemical analysis indicate that on heating, this compound could have a 15.1% weight loss. DSC analysis showed that on heating this material from 47° to 207°C, the weight loss was 13.8%.

Tests 2-2 and 2-3 were begun in the same slurry. Both orthorhombic tablets and monoclinic blades formed in the slurry with the blades so small as to pass through the filter (medium-fritted Gooch crucible) with the filtrate. The tablets then were air dried and designated as test product number 2-2 $(C_3H_6N_6)_3 \cdot H_2SO_4 \cdot 4H_2O$. The filtrate containing the blade crystals was heated until a clear solution resulted and then was allowed to cool slowly to form large blades which could be filtered. This sample was designated 2-3. Because these monoclinic blades were formed in the same slurry as a 94% sulfate salt, they may represent approximately the maximum sulfate substitution (about 65%) in the monoclinic blade salt. DSC analysis showed a loss of 15.6% versus a theoretical value of 19%.

Twenty percent of the product from test 2-5 was monoclinic plates, thought to be $(C_3H_6N_6)_2 \cdot H_2SO_4 \cdot 2H_2O$. This salt was not produced as a homogeneous product in these tests. The bulk of the product from test 2-5 (60%) consisted of melamine sulfite dihydrate with the balance as decomposing melamine sulfite tetrahydrate. DSC analysis showed a loss of 23.8% versus a theoretical 24.6%.

Test 3-1, in which the antioxidant was added, resulted in the formation, after heating to 70°C and overnight cooling, of monoclinic blade crystals. About 15% of the sulfur was in sulfate form. DSC testing resulted in 29.1% weight loss which is the theoretical value.

Test 3-2, a repeat of test 2-5 except with antioxidant added, resulted in a mixture of monoclinic blades and monoclinic rods. About 16% of the sulfur was oxidized to sulfate. DSC testing resulted in 30.2% weight loss versus a theoretical 28.2%.

The majority of the products from this series of tests consisted of monoclinic blades which were first identified in test 7-V-1. Chemical analyses of these products indicate 2 moles of melamine per mole of sulfur with approximately 2 moles of water. The degree of oxidation varied. The highest degree of oxidation appeared in the products which were allowed the longest reaction time except when an antioxidant was added to the slurry. Products exhibiting the least oxidation were from tests where antioxidant was added to the test slurry. The weight loss during DSC tests equaled or nearly equaled the calculated values.

Although the refractive indices of the monoclinic blades vary, this variation does not form a predictable pattern for determining the degree of oxidation of a particular sample. There is some indication that over a period of time there is a slight variation in the indices themselves. It is possible that this variation might be caused by small changes in the quantity of water associated with the crystals.

The DSC test curves for the three fairly pure products are shown in Figure 44. As reported earlier, the test for the monoclinic prisms, $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O$, indicates that a major portion (about 3 moles) of the water might be separated from the SO_2 on thermal decomposition. The weight loss on heating at 20°C per minute to 90°C was 9.3% and to 103°C was 13.5% (2 moles of water would be 9.5% and 3 moles of water would be 13.3%). Testing of the off-gas over this range indicated little SO_2 to be present. The remainder of the weight loss, equivalent to 1 mole of water and 1 mole of sulfurous acid, was lost between 103° and 150°C. Separation of a major portion of the water from the sulfurous acid should be possible in the proposed process.

The DSC curve for the monoclinic blade product, $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 2H_2O$, shows all the reaction to take place in one large endothermic peak. All the weight loss (2 moles of water plus 1 mole of sulfurous acid) takes place between 92° and 145°C. No separation of water from sulfurous acid by thermal decomposition is indicated.

DSC analysis of the orthorhombic tablets $(C_3H_6N_6)_3 \cdot H_2SO_4 \cdot 4H_2O$, shows the reaction to take place in three steps. Apparently the water was evolved with 1 mole being lost in heating to 100°C (about 3% wt. loss), an additional 2 moles at 150°C (about 6% wt. loss), and the last mole at about 180°C (about 5% wt. loss). No sulfur should be lost in this test since the sulfate is not volatile at the temperatures involved.

DSC test curves for the mixed products and those of major proportions of both sulfate and sulfite are exemplified by the curves in Figure 45. These curves are not definitive enough to identify the specific losses at any given temperature although the total losses are very near the theoretical values. These products would not allow separation of water from SO_2.

Recommendations

In the proposed process the crystal form most likely to be produced is the blade-type crystal $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 2H_2O$. Products consisting of this crystal habit are very slow filtering and drying, especially when compared with the filtering time of the tetrahydrate products. If the dihydrate crystals were allowed to remain in the mother liquor containing antioxidant and at temperatures of 25°C or below for a period of time to allow the tetrahydrate to form, the tetrahydrate could then be easily filtered and heated to about 103°C to drive off 3 moles of water. The remaining product could then undergo melamine regeneration and with addition of oxygen result in 84.5% H_2SO_4. The economic feasibility of such a process or of one using the dihydrate directly would need to be studied.

PRODUCTION OF MELAMINE SULFITE FROM MELAMINE AND SODIUM BISULFITE SCRUBBER LIQUORS

Exploratory operation of the minipilot plant was carried out in the mode of the sodium sulfite-melamine double reactant process (13). A sodium sulfite solution containing 0.1% p-phenylenediamine as an antioxidant was fed and the spent solution was reacted with melamine. The regenerated solution was

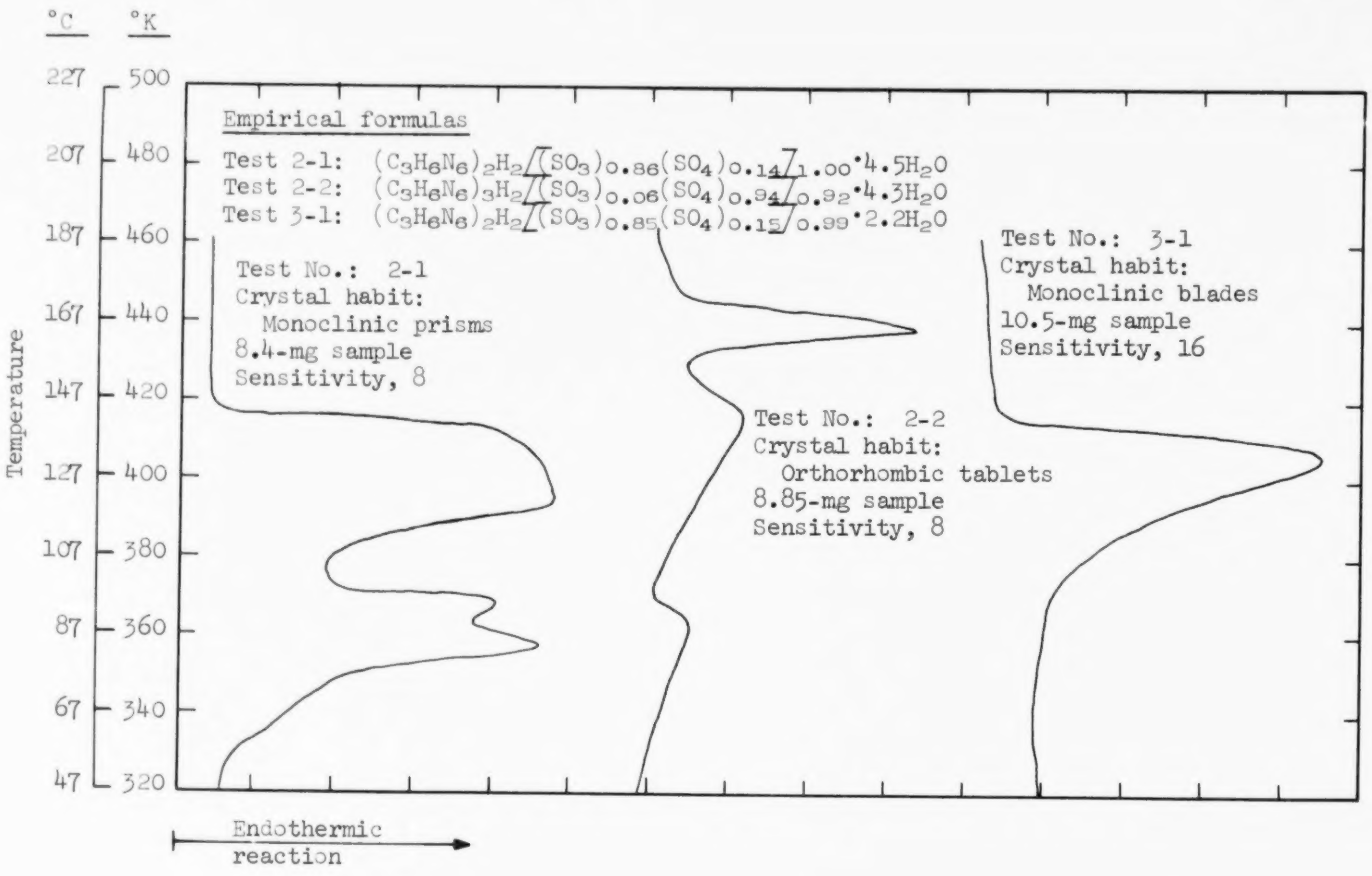
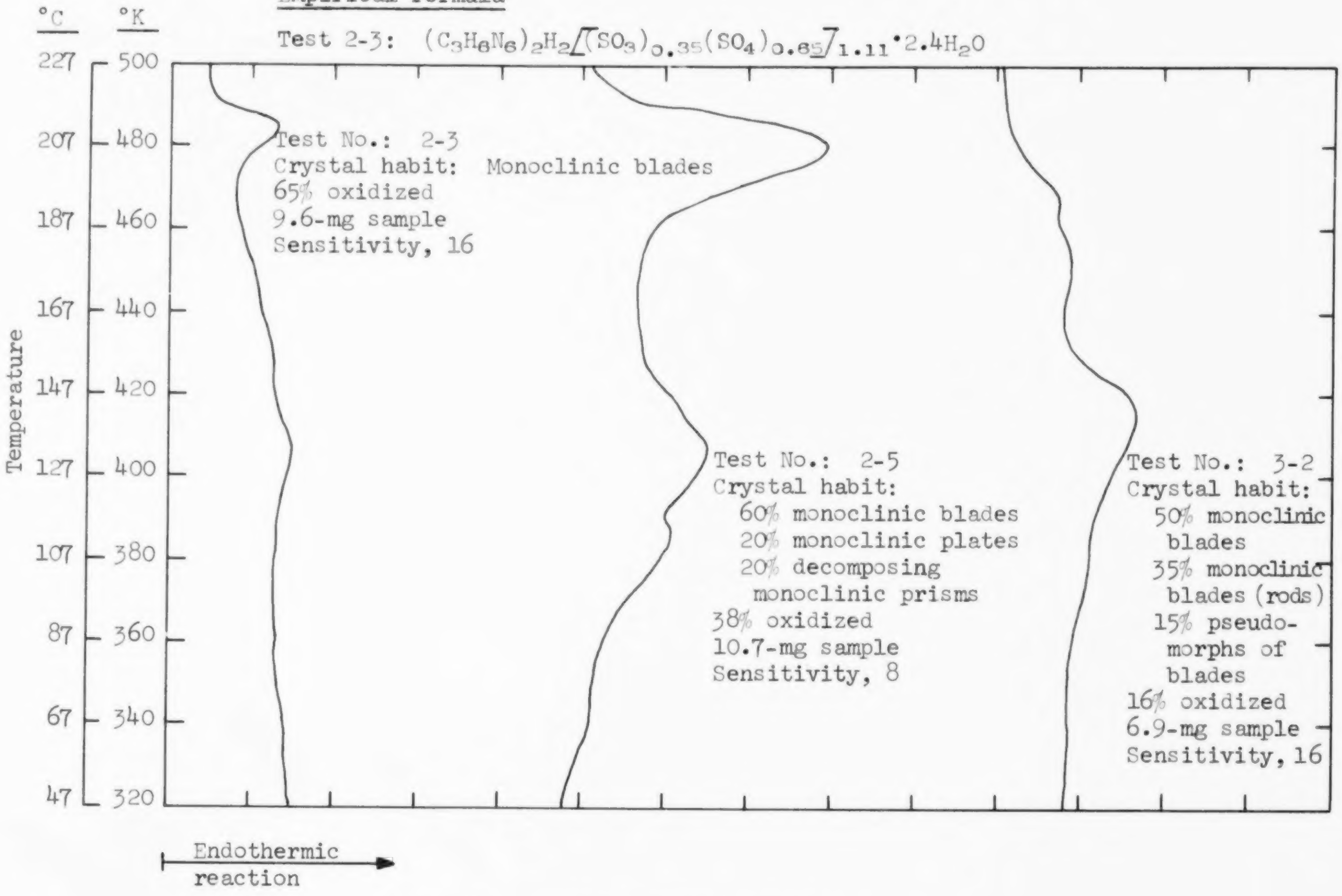


Figure 44. Sodium sulfite-melamine process--differential scanning calorimeter analysis of pure products.

Empirical formula

Test 2-3: $(C_3H_6N_6)_2H_2[(SO_3)_{0.35}(SO_4)_{0.65}]_{1.11} \cdot 2.4H_2O$



Test No.: 2-3
Crystal habit: Monoclinic blades
65% oxidized
9.6-mg sample
Sensitivity, 16

Test No.: 2-5
Crystal habit:
60% monoclinic blades
20% monoclinic plates
20% decomposing monoclinic prisms
38% oxidized
10.7-mg sample
Sensitivity, 8

Test No.: 3-2
Crystal habit:
50% monoclinic blades
35% monoclinic blades (rods)
15% pseudomorphs of blades
16% oxidized
6.9-mg sample
Sensitivity, 16

Figure 45. Sodium sulfite-melamine process--differential scanning calorimeter analysis of mixed or impure products.

recycled to the scrubber and the spent melamine was held for later recovery. In the run it was found that the use of the stoichiometric amount of melamine to react with the SO_2 in the incoming gas did not result in sufficient regeneration of sodium sulfite solution to maintain high SO_2 removal. The use of significantly greater portions of melamine did not improve the situation. Apparently, the acceptance of a low regeneration efficiency, a higher forward flow in the scrubber, and a lower pH in the scrubber would be required in a viable process. It was decided to use the spent scrubber solution collected during the latter part of the run to further study the reaction with melamine.

Eight tests were made in which the melamine stoichiometry, as illustrated by the following equation, was varied from 40% to 400%.

$$2NaHSO_3 + 2C_3H_6N_6 \longrightarrow (C_3H_6N_6)_2 \cdot H_2SO_3 \cdot xH_2O + Na_2SO_3$$

In each test 150 milliliters of the spent scrubber liquor (0.231 g/ml total sulfur, 0.228 g/ml sulfite sulfur, 0.224 g/ml bisulfite sulfur) was placed in an 8-ounce sample bottle and allowed to equilibrate in a water bath at 52°C. The desired amount of melamine then was added batchwise with constant stirring. In the first five tests the reacting slurry was left open to air (aerobic); in the last three tests the reacting slurry was covered with a nitrogen blanket and closed with a rubber stopper to minimize the effects of air contact (anaerobic). Slurry samples were taken at various time intervals throughout each test and were filtered immediately (coarse-frit funnel with glass-fiber filter paper) using a minimum of vacuum. The filter cakes were washed with ethanol (about 10 ml) and air dried for 5 minutes using the house vacuum. Microscopic examination of the dried cakes and chemical analysis of the filtrates (bisulfite sulfur) were performed by personnel of this laboratory. The slurry remaining at the end of each test was filtered using the same procedure and those filter cakes were submitted to the analytical laboratory for chemical analysis. The test data are listed in Table 28.

Results of Filtrate Analyses

The proportion of $NaHSO_3$ reacted (% of input) calculated from the analyses of the filtrate samples taken throughout each test are listed in the table. These results indicate an average of 35% of the input $NaHSO_3$ reacted at the end of all the tests. The maximum proportion reacted was 49% of input in test 8 (100% stoichiometry, anaerobic) after a total reaction time of 52 hours. In the aerobic tests, the extent of the reaction, based on the bisulfite analysis of the filtrate, never exceeded 40% but reached a maximum value and then declined before rising again as shown in Figure 46 (only four tests plotted for simplicity). The timing of the first maximum depended on the melamine stoichiometry; higher stoichiometry resulted in more rapid attainment of the maximum. Linear regression analysis gives the equation for this relationship as follows:

$$\text{Time of maximum reaction, min} = 59.74 - 0.146\ (\text{stoichiometry, }\%)$$

The correlation coefficient, 0.981, indicates a pronounced linear relationship between the variables. This relationship is shown in Figure 47. The reason for the reaction to reach an indicated maximum and then to decline is not

TABLE 28. PRODUCTION OF MELAMINE SULFITE FROM MELAMINE AND $NaHSO_3$ SCRUBBER LIQUOR--LABORATORY TESTS

Test No.	1	2	3	4	5	6	7	8
Formulation, g								
$NaHSO_3$[a]	10.9	10.9	10.9	10.9	10.9	10.9	10.9	10.9
$C_3H_6N_6$	13.2	26.5	52.9	8.0	5.3	13.2	13.2	13.2
$C_3H_6N_6$:$NaHSO_3$ mole ratio[b]	1.0	2.0	4.0	0.6	0.4	1.0	1.0	1.0
Temperature, °C	52	52	52	52	52	52	52	52
Time, min (total)	240	180	135	150	195	75	60	3300
Air contact	Yes	Yes	Yes	Yes	Yes	No	No	No
$NaHSO_3$ reacted, % of input at time indicated, min[c]								
2	-	-	33.8	23.7	17.0	-	32.6	-
15	27.7	35.3	33.1	30.4	25.9	36.6	37.5	-
30	30.8	38.8	31.3	33.9	29.0	37.1	36.2	-
45	34.8	35.3	31.7	34.4	30.4	37.1	35.7	-
60	29.0	34.4	-	-	34.8	38.4	33.0	-
75	-	34.4	-	-	34.8	35.3	-	-
105	-	33.9	-	33.9	34.4	-	-	-
135	-	-	29.5	35.3	-	-	-	-
150	-	-	-	-	-	-	-	-
180	-	37.1	-	-	33.0	-	-	-
240	32.3	-	-	-	-	-	-	38.4
420	-	-	-	-	-	-	-	45.1
1380 (23 hr)	-	-	-	-	-	-	-	45.5
1680 (28 hr)	-	-	-	-	-	-	-	47.4
1860 (31 hr)	-	-	-	-	-	-	-	42.2
3120 (52 hr)	-	-	-	-	-	-	-	49.1
3300 (55 hr)	-	-	-	-	-	-	-	44.2
Final solids[d] analysis, %								
N	50.6	59.6	63.2	48.3	41.3	51.3	47.5	52.4
S	3.9	1.6	0.80	5.3	7.8	2.9	2.7	2.9
Sulfite S	2.1	0.24	0.13	5.2	7.5	2.3	2.1	2.4
Calculated indices[e]								
$C_3H_6N_6$:S mole ratio	4.95	14.09	30.30	3.47	2.01	6.76	6.71	6.90
Residual $C_3H_6N_6$, % of solids	59.5	85.9	93.4	42.4	0.8	70.3	70.2	71.0
$NaHSO_3$ reacted, % of input[f]	40.5	28.2	26.6	34.6	39.7	29.7	29.8	29.1
S oxidized to sulfate, %	46	85	84	1.9	3.9	21	22	17

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[a] Fed as 150 milliliters of spent scrubber liquor from minipilot-plant run; contained 231 g/l total sulfur, 288 g/l sulfite sulfur, 244 g/l bisulfite sulfur.

[b] 1 mole $C_3H_6N_6$ per mole of $NaHSO_3$ is 100% stoichiometric using following equation:

$$2NaHSO_3 + 2C_3H_6N_6 \longrightarrow (C_3H_6N_6)_2 \cdot H_2SO_3 \cdot xH_2O + Na_2SO_3$$

[c] As determined from bisulfite analyses as determined by potassium iodide - iodate titration.

[d] Residual solids after filtering, washing with ethanol, and drying in air.

[e] Based on final solids analysis.

[f] Based on residual melamine proportion and stoichiometry.

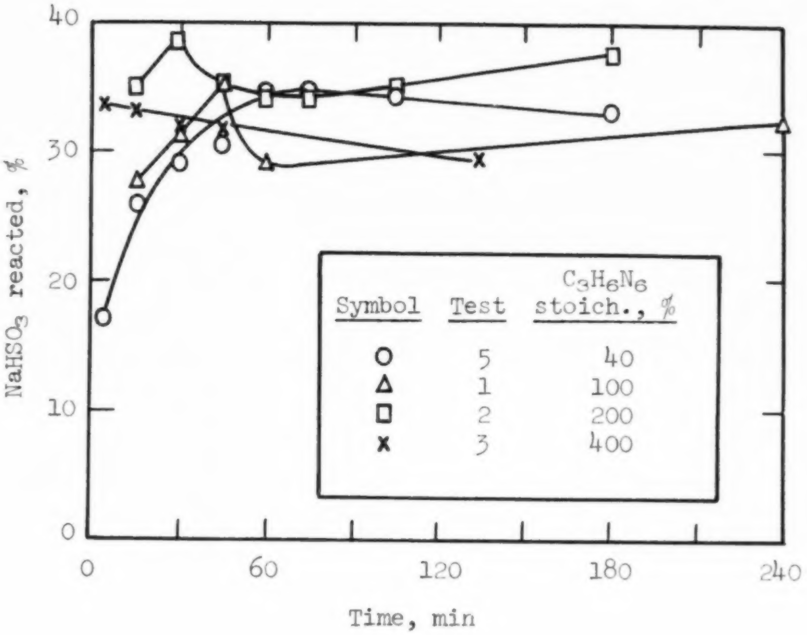

Figure 46. Production of melamine sulfite from melamine and NaHSO$_3$ scrubber liquor--proportion of NaHSO$_3$ reacted versus time.

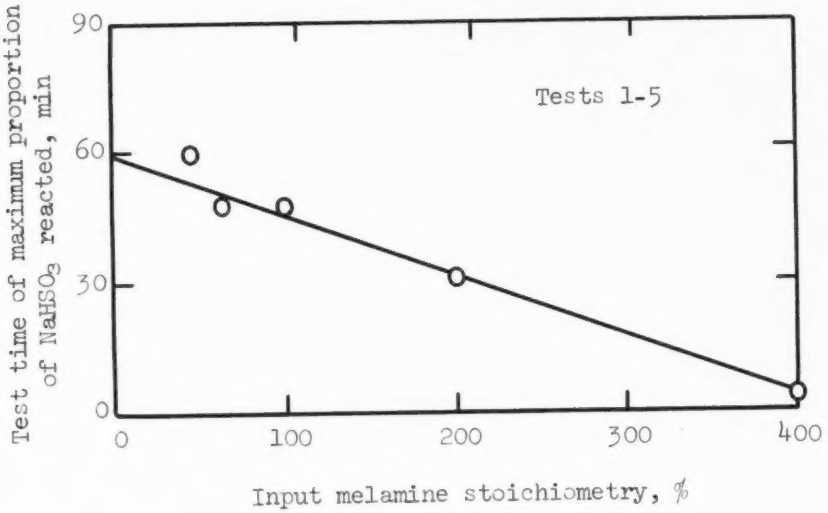

Figure 47. Production of melamine sulfite from melamine and $NaHSO_3$ scrubber solution--effect of stoichiometry on time required to reach maximum proportion of $NaHSO_3$ reacted.

understood but may be associated with oxidation to sulfate. The aerobic tests were not continued as long as test 8 in which the greatest degree of reaction was attained but were continued for about as long as could reasonably be allowed in a continuous scrubbing process.

The rates of reaction during the first 2 minutes of the aerobic tests (tests 3, 4, and 5) were 16.9, 11.8, and 8.5% when the melamine stoichiometries were 400, 60, and 40%, respectively. The pH rise for the same periods (from the initial 4.8) were 0.9, 0.8, and 0.7, respectively. These data indicate the effect of melamine stoichiometry on rate; increased amounts of melamine increased the rate of bisulfate reaction but not the extent.

The three anaerobic tests (6, 7, and 8) were made at 100% melamine stoichiometry with the time of the tests being the only intentional variable. Tests 6 and 7 were continued for 60 and 75 minutes, respectively. Results were essentially parallel; excepting the analyses at 60 minutes, the values for proportion of bisulfite reacted varied less than 1.4%. Test 8 was a longer term test. It was analyzed first at 240 minutes and was maintained for 3300 minutes (55 hr). The degree of reaction of the bisulfite became fairly constant at about 45% after 7 hours.

Results of the Final Filter Cake Analyses

The chemical analyses of the final filter cakes and the indices calculated from those analyses are listed in Table 28. It is noted that these results show some variations from the $NaHSO_3$ proportions reacted calculated from the filtrate analyses. These variations probably result from the calculations having been based on the bisulfite sulfur in one case but based on the residual melamine proportion in the other case. Except in test 8 (55 hr) the values varied less than 10 percentage points.

The proportion of sodium bisulfite equivalent reacted in the final filter cake (calculated from the total sulfur analysis) averaged 34% for aerobic tests and averaged 30% for the anaerobic tests. The range of values for the aerobic tests was from 27% in test 3 to 41% in test 1. The range in the anaerobic tests was less than 1% (29.5±0.4).

The effect of stoichiometry on the $C_3H_6N_6$:S mole ratio in the solids can be illustrated by Figure 48. This plot shows that the $C_3H_6N_6$:S mole ratio in the cake increased linearly with an increase in the input melamine stoichiometry. The equation of the line (using the results from all eight tests) is:

$$C_3H_6N_6:S \text{ mole ratio in filter cake} = 0.080 (\% \text{ stoichiometry}) - 1.46$$

The correlation coefficient, 0.998, indicates the high probability of a linear relationship between the variables and that the low stoichiometry (40%) did not adversely affect the degree of reaction.

It was noted also that increasing the stoichiometry generally resulted in increased oxidation of sulfur. The proportion of sulfur oxidized reached a maximum of 85% at 200% stoichiometry and held that level at 400% stoichiometry. This result can be illustrated by a graph of sulfur oxidation versus

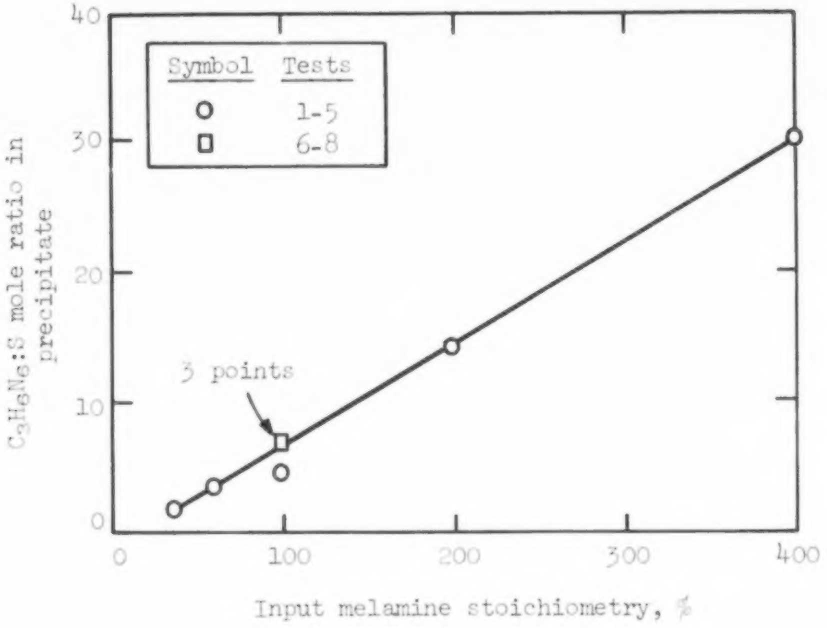

Figure 48. Production of melamine sulfite from melamine and $NaHSO_3$ scrubber liquor--effect of stoichiometry on $C_3H_6N_6$:S mole ratio in the final filter cake.

stoichiometry as in Figure 49. These results indicate a possible preferential reaction with sulfite sulfur (also noted in the previous work with reagent-grade materials). The effect of keeping air away from the slurry at the 100% stoichiometric level was a 57% decrease in sulfur oxidized.

Results of Microscopic Examination

Microscopic examination of the solid samples taken throughout each test revealed that at least three phases were present in addition to melamine. Two of these phases were identified as $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O$ and $(C_3H_6N_6) \cdot H_2SO_3 \cdot 2H_2O$. The third appears to be the $(C_3H_6N_6)_2 \cdot H_2SO_3 \cdot 4H_2O$ salt having a different crystalline habit. All probably had some degree of sulfate substitution. The proportion of each phase varied greatly between some tests but was similar for other tests. However, no correlation between the phase or phases precipitated and any of the test conditions was noted.

Conclusions

Under the conditions used in these tests, it was determined that an average of about 33% of the input $NaHSO_3$ reacted with the melamine added. It was found that increasing the melamine stoichiometry resulted in (1) an increase in the $C_3H_6N_6$:S mole ratio in the final filter cake, (2) an increase in sulfur oxidized in the final filter cake, and (3) an increase in the rate of reaction. Also, keeping the reaction slurry from contact with air significantly reduced the proportion of sulfur oxidized at 100% stoichiometry. The test results were reproducible within reasonable accuracy.

The results most adaptable to the proposed double reactant process were obtained in test 5 in which 40% stoichiometric melamine was added. A product containing less than 1% free melamine was obtained in which oxidation was less than 4%. The regeneration of such material would be much less expensive than products containing more melamine and higher degrees of oxidation. Operating in this manner would require higher forward flow rates through the scrubber circuit, however, and the scrubber efficiency would have to be greater than if a scrubber feed solution containing little or no bisulfite could be produced.

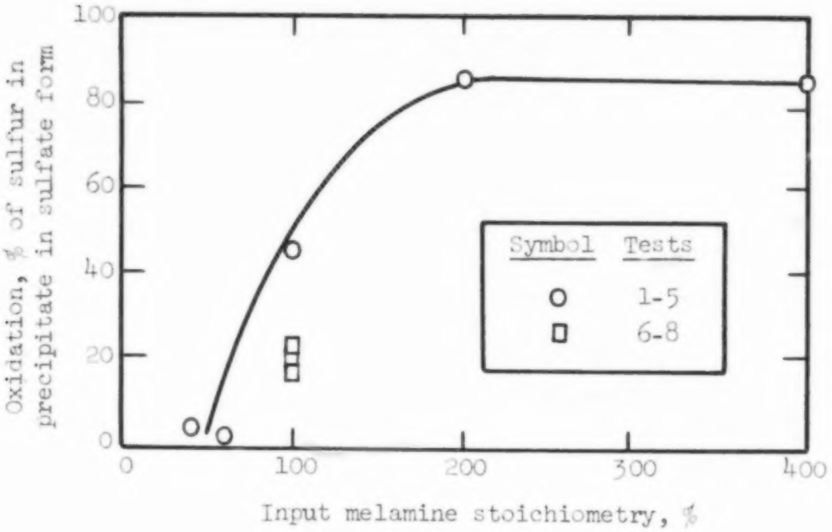

Figure 49. Production of melamine sulfite from melamine and $NaHSO_3$ scrubber liquor--effect of stoichiometry on sulfur oxidation in the final filter cake.

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